APPENDIX 10

ENVIRONMENTAL STANDARDS, INC.
DATA VALIDATION SOPs

TABLE 14-1
ITEMS REVIEWED DURING ENVIRONMENTAL STANDARDS, INC.'s QUALITY ASSURANCE REVIEWS

Areas Examined	Applicability (organic, inorganic, both)
Field and laboratory Chain-of-Custodies (field notes, etc.) Laboratory narrative and QC summaries	Both
Holding times	Both
Extraction/digestion logs	Both
Blanks - field & laboratory (accuracy)	Both
Instrument tune	Organic
Standards	Both
Linearity	Both
Sensitivity/stability	Both
Selectivity/specificity	Both
EPA criteria	Both
Variability of technique (internal standards)	Organic
ICP interference	Inorganic
Analyte breakdown	Organic
Analytical sequence	Organic
Control standards	Inorganic
Serial Dilutions	Inorganic

TABLE 14-1 (Cont.)

ITEMS REVIEWED DURING ENVIRONMENTAL STANDARDS, INC.'s

QUALITY ASSURANCE REVIEWS

Areas Examined	Applicability (organic, inorganic, both)
Samples	
Detection limits	Both
Instrument printouts	Both
ICP data	Inorganic
AA data	Inorganic
GC data	Organic
GC/MS data	Organic
Autoanalyzer data	Inorganic
Qualitative Identification	Both
Mass spectra	Organic
Herbicide results	Organic
Tentatively identified compounds	Organic
Quantitative Reliability	Both
Calculations/equations	Both
Matrix spikes (accuracy) Bias	Both
Matrix spike duplicates Bias Accuracy and precision	Organic
Surrogate spikes Bias	Organic

TABLE 14-1 (Cont.)
ITEMS REVIEWED DURING ENVIRONMENTAL STANDARDS, INC.'s QUALITY ASSURANCE REVIEWS

Areas Examined	Applicability (organic, inorganic, both)
Samples (Cont'd)	
Duplicates (field & laboratory) Precision Representativeness	Both
Post-digestion spikes (graphite furnace AA) Matrix effects	Inorganic

STANDARD OPERATING PROCEDURES FOR DATA VALIDATION OF VOLATILE ORGANICS BY SW-846 METHOD 8260A*

I. METHOD SUMMARY

Water Samples

The volatile compounds are introduced into the gas chromatography by the purge-and-trap method or by direct injection (in limited applications). Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components. The analytes are desorbed directly to a large bore capillary column GC or cryofocussed on a capillary precolumn before being flash evaporated to a narrow bore capillary column GC for analysis. The column is temperature programmed to separate the analytes which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph. Wide bore capillary columns require a jet separator, whereas narrow bore capillary columns can be directly interfaced to the ion source.

Soil/Sediment Samples

Low level - an inert gas is bubbled through a mixture of reagent water and 5 g of sample prior to purging. The analysis then proceeds as described above.

Medium level - a measured amount of soil is extracted with methanol. A portion of the methanol extract is diluted to 5 mL with reagent water. This solution is then subjected to GC/MS analysis following purge and trap, as described above.

II. TECHNICAL HOLDING TIMES

A. Review Items

Form I VOA, Chain-of-Custody Records, raw data, and Case Narrative

B. Objective

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* **See Section XV for Authority and Application of this SOP.**

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of analysis.

C. Criteria

Technical requirements for sample holding times have only been established for water matrices. The holding time criteria for water samples are as follows:

For non-aromatic volatile compounds in cooled (at 4±2° C) water samples, the maximum holding time is 14 days from sample collection.

For purgeable aromatic hydrocarbons in cooled (at 4±2° C), acid-preserved (pH 2 or below) water samples, the maximum holding time is 14 days from sample collection.

For purgeable aromatic hydrocarbons in cooled water (4±2°C) samples that have not been maintained at 4°C and preserved to a pH of 2 or below, the maximum holding time is 7 days from sample collection.

For solid samples, the maximum holding time is 14 days from sample collection.

D. Evaluation Procedure

Technical holding times are established by comparing the sampling dates on the Chain-of-Custody Records with the dates of analysis on the VOA Form I's and the raw data. Examine the sample records to determine if samples were preserved.

E. Action

If technical holding times are exceeded, document in the quality assurance review that holding times were exceeded and qualify the sample results according to the following criteria:

1. Unpreserved Aqueous Samples:

   a. For aromatic compounds (listed below) in unpreserved (pH > 2) water samples analyzed more than 7 days but up to 14 days from

sample collection, flag positive aromatic sample results as estimated (flagged "J") and flag "not-detects" as "UJ".
For non-aromatic compounds in unpreserved (pH>2) samples analyzed more than 14 days but up to 28 days from time of sample collection, flag positive sample results as estimated (flagged "J") and "not-detects" as "UJ".

b. For aromatic compounds (listed below) in unpreserved (pH>2) water samples analyzed more than 14 days from the date of sample collection, flag all positive results as estimated (flagged "J") and "not-detects" as "R".

For non-aromatic compounds in unpreserved (pH>2) water samples analyzed more than 28 days from the date of sample collection, flag positive results as estimated (flagged "J") and "not-detects" as "R".

2. Preserved aqueous samples:

a. For aqueous samples analyzed more than 14 days and less than 28 days from the time of sample collection, flag all positive sample results as estimated (flagged "J") and "not-detects" as "UJ".

b. For aqueous samples analyzed more than 28 days from the time of sample collection, flag all positive samples results as estimated (flagged "J") and "not-detects" as "R".

3. Solid samples:

a. For solid samples analyzed more than 14 days and less than 28 days from the time of sample collection, flag all positive sample results as estimated (flagged "J") and "not-detects" as "UJ".

b. For solid samples analyzed more than 28 days from the time of sample collection, flag all positive samples results as estimated (flagged "J") and not-detects" as "R".

Aromatic Volatile Compounds

benzene	1,4-dichlorobenzene
chlorobenzene	ethylbenzene
1,2-dichlorobenzene	toluene
1,3-dichlorobenzene	xylenes

4. If a sample is received at the laboratory with a temperature greater than 6°C but less than or equal to 10°C, and the temperature of the cooler was measured with an IR gun or with a temperature bottle, flag positive results for all compounds as estimated ("J") and all "not-detected" results "UJ". In addition, note the deficiency in the quality assurance report.

5. If a sample is received at the laboratory with a temperature greater than 10°C and the temperature of the sample cooler was measured with an IR gun or with a temperature bottle, flag all positive results as estimated ("J") and all "not-detected" results as unusable ("R"). In addition, note the deficiency in the quality assurance report.

6. If high temperatures were noted for project samples, but the laboratory used a method other than temperature bottles or IR guns for measuring the cooler temperatures, comment in the report that high sample temperatures were noted but that the method of measuring the cooler temperature may not reflect actual sample temperatures, and data was not qualified based on this issue. In addition, note if the laboratory indicated the presence of wet ice or blue ice in the sample cooler.

III. GC/MS TUNING

A. Review Items

Form V VOA, bromofluorobenzene (BFB) mass spectra, and mass listing

B. Objective

GC/MS tuning is performed to ensure mass resolution, identification, and to some degree, sensitivity. These criteria are not sample specific and should be met in all circumstances.

C. Criteria

The analysis of the tune must be performed at the beginning of each 12-hour period during which samples or standards are analyzed. The instrument performance check compound, BFB for volatile analysis, must meet the ion abundance criteria given below. Note that alternate tuning criteria (Method 625, CLP, etc.) is acceptable as long as method performance is not adversely affected.

BROMOFLUOROBENZENE (BFB)

m/z	ion abundance criteria
50	15-40% of mass 95
75	30-60% of mass 95
95	base peak, 100% relative abundance
96	5-9% of mass 95
173	less than 2% for mass 174
174	greater than 50% of mass 95
175	5-9% of mass 174
176	greater than 95%, but less than 101% of mass 174
177	5-9% of mass 176

Note: All ion abundances must be normalized to mass 95, the nominal base peak, even though the ion abundance of mass 174 may be greater than that of mass 95.

D. Evaluation

1. Compare the data presented for each tune with each mass listing submitted to ensure the following:

   a. Form V is present and completed for each 12-hour period during which samples were analyzed.

b. The laboratory has not made transcription errors between the data and the form.

c. The laboratory has not made calculation errors.

2. Verify from the raw data that the mass alignment is correct and that the mass listing is normalized to mass 95.

3. Verify that the ion abundance criteria was met. The criteria for mass 173, 175, 176, and 177 are calculated normalizing to the specified mass.

4. All instrument conditions must be identical to those used in the sample analysis.

E. Action

1. If the laboratory has made minor transcription errors which do not significantly affect the data, the data reviewer should make the necessary corrections on a copy of the form.

2. If the laboratory has failed to provide the correct forms or has made significant transcription or calculation errors, the reviewer must use professional judgment to assess the data.

3. If mass assignment is in error (such as mass 96 is indicated as the base peak rather than mass 95), qualify all associated data as unusable (flagged "R").

4. If ion abundance criteria are not met, professional judgment may be applied to determine to what extent the data may be utilized. The critical ion abundance criteria for BFB are the mass 95/96, 174/175, 174/176, and 176/177 ratios.

5. Decisions to use analytical data associated with BFB tune not meeting contract requirements should be clearly noted in the quality assurance review.

6. If the reviewer has reason to believe that the tuning criteria were achieved using techniques other than those described, additional information on the tuning should be obtained.

IV. INITIAL CALIBRATION

A. Review Items

Form VI VOA, quantitation reports, and chromatograms

B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for target compounds.

C. Criteria

1. After the GC/MS tuning and mass calibration, the instrument must be calibrated prior to sample analysis. The initial calibration is performed with at least five standards, one of which should contain each analyte at a concentration at or near the method detection limit for that compound; the other calibration standards should contain the analytes at concentrations which define the working range of the instrument. Introduction of the samples into the instrument should be performed in the same manner as will the samples.

2. The average relative response factor for each compound must be calculated and recorded using the five relative response factors for each compound from the 5-point calibration curve. Five System Performance Check Compounds (SPCCs) are checked for minimum average relative response factors. These criteria must be met before samples can be analyzed. If the criteria are not met, the laboratory must correct the problem and recalibrate the instrument.

   The minimum relative response factor for volatile SPCCs are as follows:

chloromethane	0.10
1,1-dichloroethane	0.10
bromoform	0.10
chlorobenzene	0.30
1,1,2,2-tetrachloroethane	0.30

3. Separate initial calibrations must be performed for aqueous samples (or medium-level soil samples) and for low-level soil samples.

4. The relative response factors (RRFs) for all volatile target compounds in the initial calibration should be greater than 0.050.

5. The percent relative standard deviation (% RSD) from the initial calibration must be <30% for each individual CCC. The CCCs are: 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride.

   If a %RSD greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is required before reattempting calibration.

   If the %RSD of any compound is 15% or less, then the relative response factor is assumed to be constant over the calibration range, and the average relative response factor may be used for any quantitation.

   If the %RSD of any compound is greater than 15%, the laboratory must construct calibration curves of area ratio (A/A_{is}) versus concentration using second or higher order regression fit of the five calibration points.

D. Evaluation

1. Verify that the correct concentrations of standards were used for the initial calibration.

2. Verify that the correct initial calibration was used for aqueous and medium-level soil samples (unheated purge) and for low-level soil samples (heated purge).

3. If any sample results were calculated using an initial calibration, verify that the correct standard (i.e., the 50 µg/L standard) was used for calculating sample results and that the samples were analyzed within 12 hours of the associated tune.

4. Evaluate the initial calibration RRFs for all volatile target compounds.

a. Check and recalculate the RRFs and average RRFs for at least one volatile target compound associated with each internal standard; verify that the recalculated value(s) agrees with the laboratory reported value(s). If errors are detected in the calculations, perform a more comprehensive recalculation.

b. Verify that for all volatile SPCCs, the initial calibration average RRFs are greater than or equal to the proper criteria. In addition, verify that all other compounds display RRFs greater than 0.050.

5. Evaluate the %RSD for all volatile target compounds.

a. Check and recalculate the %RSD for one or more volatile target compound(s) and verify that the recalculated value(s) agrees with the laboratory reported value(s). If errors are detected in the calculations, perform a more comprehensive recalculation.

b. Verify that all volatile target compounds have a %RSD less than or equal to 30.0%.

E. Action

1. If any volatile target compound result has an average relative response factor of less than 0.050:

a. Flag positive results for that compound as estimated (flagged "J").

b. Flag "not-detects" for that compound as unusable ("R").

2. If any volatile target compound has a %RSD greater than 15% and the laboratory used a linear calibration curve or the average relative response factor for quantitation of a positive result for that compound:

a. Flag positive results for that compound as estimated (flagged "J").

b. "Not-detects" for that compound may be qualified using professional judgment.

3. If the initial calibration did not meet all criteria for the CCCs and the SPCCs, note the deficiency in the report. Validate all data based on the criteria stated in E.1. and E.2. above.

V. CONTINUING CALIBRATION

A. Review Items

Form VII VOA, quantitation reports, and chromatograms

B. Objective

Continuing calibration establishes the 12-hour relative response factors on which the quantitations are based and checks satisfactory performance of the instrument on a day-to-day basis.

C. Criteria

1. The initial calibration curve for each compound of interest must be checked and verified once every 12 hours during analysis with the introduction technique used for samples. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the System Performance Check Compounds (SPCC) and the calibration check compounds (CCC). A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of relative response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum relative response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins.

2. The continuing calibration RRFs for volatile target compounds must be greater than or equal to 0.050.

3. The percent drift (%D) between the average initial calibration responses and the concentration of the compounds determined in the continuing calibration must be within the ±20%.

4. Verify that the SPCCs meet all of the relative response factor criteria as stipulated for the initial calibration.

D. Evaluation Procedure

1. Verify that the continuing calibration was run at the required frequency and that the continuing calibration was compared to the correct initial calibration.

2. Evaluate the continuing calibration RRF for 10% of the volatile target compounds (at least one per internal standard):

   a. Check and recalculate the RRF for at least one volatile target compound associated with each internal standard and verify that the recalculated value(s) agrees with the laboratory reported value(s). If errors are detected in the calculations of the RRFs, perform a more comprehensive recalculation.

   b. Verify that for all volatile target compounds, the initial calibration average RRFs are > 0.05.

3. Evaluate the % Drift between the responses from the initial calibration and the concentration calculated from the continuing calibration for all compounds.

   Calculate the percent drift using the following equation:

   $$\% \text{ Drift} = (C_I - C_C) / C_I \times 100$$

   where :

   C_I = Calibration Check Compound standard concentration.

   C_c = Measured concentration using selected quantitation method.

   If the percent drift for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met ($>$ 20% drift), for any one CCC, corrective action must be taken. If no source of the problem can be determined after corrective action have been taken, a

new five point calibration MUST be generated. This criterion MUST be met before quantitative sample analysis begins. In addition, if the CCCs are not target analytes for the particular analysis, then all target analytes must display % drifts of 20% or less.

E. Action

1. If any volatile compound result has a relative response factor of less than 0.050:

   a. Flag positive results for that compound as estimated (flagged "J").

   b. Flag "not-detects" for that compound with an "R."

2. If any volatile target compound has a %D greater than 25.0%:

   a. Flag positive results for that compound as estimated (flagged "J").

   b. "Not-detects" for that compound may be qualified using professional judgment.

3. If the continuing calibration failed any of the criteria for the CCCs or SPCCs and the laboratory did not terminate the analysis and recalibrate the instrument, note the deficiency in the quality assurance report. Qualify all data based on the criteria of E.1 and E.2 above.

VI. BLANKS

A. Review Items

Blank Form I VOA, Form IV VOA, chromatograms, and quantitation reports

B. Objective

The assessment of blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with any blank

exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. See the QAPP for project-specific information regarding field, trip, and equipment blanks.

C. Criteria

1. The method requires only a laboratory blank to be analyzed after a sample analysis which saturates the instrument due to high levels of target or non-target compounds. This blank must be free of interferences or the system must be decontaminated. Samples may not be analyzed until the blank analysis is demonstrated to be free of interferences.

2. Most (if not all) laboratories will analyze a method blank after the continuing calibration and before sample analysis. The method blank should be analyzed on each GC/MS system used to analyze samples for each type of analysis [i.e., unheated purge (aqueous and medium-level solid samples) and heated purge (low-level solid samples)]. This method blank should not display target compounds at levels greater than the reporting limits (except for the common laboratory contaminants which should display levels less than five times the reporting limit).

D. Evaluation Procedure

1. Review the results of all associated blanks on the forms and raw data (chromatograms and quantitation reports) to evaluate the presence of target and non-target compounds in the blanks.

2. Verify that if a sample saturates the instrument, the laboratory followed this analysis with laboratory blanks and these laboratory blanks displayed no interferences.

E. Action

Positive sample results are not qualified for associated blank contamination unless the concentration of the compound in the sample is less than or equal to 10 times (10×) the amount in any blank for the common volatile laboratory contaminants listed below or 5 times (5×) the amount for other volatile target

compounds. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant. The results must not be corrected by subtracting any blank value.

Comment Volatile Laboratory Contaminants

methylene chloride

acetone

2-butanone

Specific actions are as follows:

1. If a volatile compound is found in a blank but not found in the sample, no action is taken.

2. If the sample result is greater than the reporting limit (RL), but less than the required amount (5× or 10×) from the blank result, the sample results are qualified as "not-detects" (flagged "U").

3. If the sample result is positive, but less than the RL, and is less than the required amount (5× or 10×) from the blank result, the result is raised to the RL and is flagged "U" ("not-detects").

4. If the sample result is greater than the required amount (5× or 10×) from the blank result, the sample results are not qualified.

5. If gross contamination exists (i.e., saturated peaks by GC/MS), all affected compounds in the associated samples should be qualified as "R" due to interference.

6. The same consideration given to the target compounds should also be given to tentatively identified compounds (TICs) that are found in both the sample and associated blank(s).

VII. SURROGATE RECOVERY

A. Review Items

Form II VOA, quantitation reports, and chromatograms

B. Objective

Laboratory performance on an individual sample is established by means of spiking activities. All samples are spiked with surrogate compounds prior to sample purging.

C. Criteria

1. Typically, three or four surrogate compounds (1,2-dichloroethane-d_4, dibromofluoromethane, bromofluorobenzene and/or toluene-d_8) are added to all samples and blanks to measure their recovery in environmental samples in sample and blank matrices.

2. Recoveries for surrogate compounds in volatile sample and blanks should be within the limits specified below. If not, the laboratory must reextract (medium-level analysis) and reanalyze the samples.

SURROGATE COMPOUND CRITERIA

Surrogate	Water %R	Solid %R
toluene-d_8	88-110	81-117
bromofluorobenzene	86-115	74-121
1,2-dichloroethane-d_4	76-114	80-120

D. Evaluation Procedure

1. Check raw data (i.e., chromatograms and quantitation reports) to verify the recoveries on the surrogate recovery Form II. Check for any calculation or transcription errors.

2. The following should be determined from the Surrogate Recovery Form(s):

a. If any surrogate compound in the volatile fraction is out of specification, there should be a reanalysis to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies.

b. The laboratory failed to perform appropriately if surrogate compounds are outside criteria with no evidence of re-analysis.

c. Verify that no blanks have surrogate compounds outside the criteria.

E. Action

Data are qualified based on surrogate compound results if the recovery of any volatile surrogate compound is out of specification. For surrogate compound recoveries out of specification, the following approaches are suggested:

1. If any surrogate compound in the volatile sample has a recovery greater than the upper acceptance limit:

   a. Positive results for volatile target compounds are qualified as estimated (flagged "J").

   b. Results for "not-detected" volatile target compounds should not be qualified.

2. If a surrogate compound in the volatile sample has a recovery greater than or equal to 10% but less than the lower acceptance limit:

   a. Positive volatile target compounds are qualified as estimated (flagged "J").

   b. Results for "not-detected" volatile target compounds should be qualified "UJ."

3. If a surrogate compound in the volatile sample has a recovery less than 10%:

   a. Positive volatile target compounds are qualified as estimated (flagged "J").

b. Results for "not-detected" volatile target compounds should be qualified "R."

4. If, upon re-analysis, the recovery is again not within limits, flag the data as estimated (flagged "J" or "UJ").

VII. MATRIX SPIKE/MATRIX SPIKE DUPLICATES

A. Review Items

Form III, chromatograms, and quantitation reports

B. Objective

Data for matrix spike/matrix spike duplicates (MS/MSD) are generated to determine long-term precision and accuracy of the analytical method on various matrices and demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone are used to evaluate the precision and accuracy of other samples.

C. Criteria

MS and MSD samples should be analyzed at a frequency of one MS and MSD per 20 samples per analytical batch. It should be noted that an MS/MSD analysis is not required by Method 8260A. Refer to the QAPP for project-specific requirements for the MS/MSD.

D. Evaluation

1. Verify transcriptions from raw data and verify calculations.

2. Compare %RSD results of nonspiked compounds for the unspiked sample and the MS and MSD samples.

3. Verify that all observed recoveries for the spiked compounds are within the reported criteria. In addition, verify that the percent differences for the spiked compounds are less than the reported quality control criteria.

E. Action

1. No action is taken on MS/MSD data alone. However, using informed professional judgment, the data reviewer may use the MS and MSD results in conjunction with the other QC criteria and determine the need for some qualification of the data.

2. In the instance where it can be determined that the results of the MS/MSD affect only the sample spiked, then the following criteria should be used for the sample that was spiked:

   a. If the recovery of a matrix spike compound in the volatile MS and/or MSD has a recovery greater than the reported upper acceptance limit (or 130%, whichever is more strict), positive results for that compound in the unspiked sample should be considered estimated (flagged "J").

   b. If the recovery of a matrix spike compound in the volatile MS and/or MSD has a recovery less than 50% (or the laboratory's lower reporting limit, whichever is more strict) and greater than 10%, the positive result for that compound in the unspiked sample should be considered estimated (flagged "J" or the "not-detected" result should be flagged "UJ").

   c. If the recovery of a matrix spike compound in the volatile MS and/or MSD has a recovery less than 10%, "not-detected" results should be flagged "R."

   d. If MS/MSD pairs exceed the specified RPD (20%; aqueous, and 40% solid), positive results for that compound should be considered estimated (flagged "J").

3. If the RSD between results for unspiked compounds in the MS/MSD exceeds 20% for aqueous samples (40% for solid samples) and all results in the MS/MSD and unspiked sample are greater than 5× the reporting limit, flag the positive result in the unspiked sample as estimated ("J").

4. If the range of results for unspiked compounds among the MS/MSD and unspiked aqueous sample exceeds the reporting limit (2×RL for solid

samples) and at least one of the results is less than 5× the RL, flag the positive result for the unspiked compounds as estimated ("J").

VIII. LABORATORY CONTROL SAMPLES

A. Review Items

LCS summary forms, quantitation reports, and chromatograms

B. Objective

To establish and document the laboratory's ability to generate acceptable precision and accuracy for each target compound in the analysis.

C. Criteria

1. The laboratory is required to analyze of the laboratory control sample (LCS) to demonstrate acceptable performance, as displayed by the recoveries for the target compounds. The frequency of the LCS analysis is not stipulated in the method; it is recommended that one series of LCS analyses is performed per batch of samples or per 20 samples, whichever is more frequent.

2. The recoveries for the target compounds must be within the ranges specified below:

Spike Compound	Recovery Range
1,1-dichloroethene	70-143%
trichloroethene	76-121%
chlorobenzene	81-121%
toluene	79-122%
benzene	79-125%

3. If the recovery criteria is not met for any compound, the laboratory must perform corrective action as stipulated in the laboratory QAPP. Possible corrective actions include:

a. The laboratory may reanalyze all samples and the LCS and report the results for all target compounds.

b. The laboratory may reanalyze all samples and the LCS and report only the results for the target compounds which failed the recovery criteria in the first series of LCS analyses. However, if failing recoveries are again observed, the laboratory must reanalyze the samples and the LCS for all target compounds.

4. It should be noted that site-specific QAPPs may stipulate criteria for the frequency, %RSDs, recoveries, and corrective actions for the LCS analyses which are different than those stated in the method. In such cases, determine laboratory performance based on the requirements of the QAPP rather than the method.

D. Evaluation

1. Verify the transcriptions from the raw data to the summary forms. Recalculate 10% of the reported results (concentrations, recoveries, and RSDs) to verify that the results were quantitated correctly.

2. Verify that all recoveries for all target compounds are within the ranges stipulated above.

3. Verify that all RSDs are less than the limits provided in the method for the target compounds.

4. If any of the recoveries in the LCS analysis exceeded the stated limits, verify that the laboratory either reanalyzed the LCS for all target compounds or reanalyzed the LCS for only those compounds which displayed unacceptable results. If the laboratory performed the latter, and failing LCS results were again observed, verify that the laboratory then reanalyzed the LCS for all target compounds.

E. Action

The results for the LCS analysis are used to qualify data for all samples associated with the LCS. If more than one series of LCS analyses are performed for one SDG, use the analysis run logs and sample preparation logs

(if provided) to determine which samples are associated with which LCS analysis.

1. If unacceptable recoveries were observed for any target compound in the LCS analysis and the laboratory did not perform the corrective action as required, include a note of this deficiency in the quality assurance report.

2. If extensive transcription errors or missing data is noted during the review of the data package, the laboratory should be contacted to provide the missing data or resubmit corrected forms.

3. If at least one recovery (out of four LCS aliquot analyses) for a target compound is outside the stated criteria, flag all positive results for that compound in all associated samples as estimated ("J").

4. If at least one recovery for a target compound is less than the lower recovery limit but greater than or equal to 10%, flag all "not-detected" results for the compound in the associated samples as estimated ("UJ").

5. If at least one recovery for a target compound is less than 10%, flag all "not-detected" results for the compound in all associated samples "R" and the analysis for the compound in all associated samples should be considered unusable.

6. "Not-detected" results for compounds displaying high recoveries in the LCS analysis are not necessarily qualified.

IX. INTERNAL STANDARDS

A. Review Items

Form VIII, quantitation reports, and chromatograms

B. Objective

Internal standards performance criteria ensure that GC/MS sensitivity and response is stable during every analysis.

C. Criteria

1. Every standard sample and blank must be spiked with internal standard compounds. Recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4.

2. Internal standard area counts in the continuing calibration must not vary by more than a factor of two (-50% to +100%) from the previous continuing calibration standard or initial calibration standard of the same concentration.

3. The retention times of the internal standards in the continuing calibration standard of the same concentration must not vary more than ±30 seconds from the previous continuing calibration standard or the initial calibration standard of the same concentration.

4. If a continuing calibration standard displays unacceptable retention times or area counts for one or more internal standards, the laboratory must correct the problem, reanalyze the continuing calibration standard, and reanalyze all samples associated with the failing continuing calibration standard.

5. It should be noted that the aforementioned retention time and area count requirements apply only to the continuing calibration standard. The method does not require reanalysis for samples which display unacceptable retention times or area counts for the internal standards. However, most laboratories will reanalyze samples with unacceptable internal standard responses to verify matrix effects. In addition, site-specific QAPPs will often state requirements for the responses for internal standards in the project samples.

D. Evaluation Procedure

1. Check raw data (e.g., chromatograms and quantitation lists) to verify the internal standard retention times and areas reported on the Internal Standard Area Summary Forms (Form VIII VOA).

2. Verify that all retention times and internal standard areas are within criteria.

3. If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations should include:

   a. Magnitude and direction of the internal standard area shift.

   b. Magnitude and direction of the internal standard retention time shift.

   c. Technical holding times.

   d. Comparison of the values of the target compounds reported in each fraction.

   e. Other quality control (QC) data results.

E. Action

1. If an internal standard area count for a sample or blank is outside -50% or +100% of the area for associated standard:

   a. Positive results for compounds quantitated using that internal standard should be qualified as estimated (flagged "J").

   b. "Not-detected" results reported using an internal standard area count less than -50% or greater than +100% are reported as the associated quantitation limit and qualified "UJ."

   c. If extremely low area counts are reported (<25%), or if performance exhibits a major abrupt drop-off, then a severe loss of sensitivity is indicated. "Not-detected" target compounds should then be qualified as unusable (flagged "R").

2. If an internal standard retention time varies by more than 30 seconds, the chromatographic profile for that sample must be examined to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection of that data for that sample fraction. Positive results should not need to be qualified as "R" if the mass spectral criteria are met.

X. TARGET COMPOUND IDENTIFICATION

A. Review Items

Form I, quantitation reports, mass spectra, and chromatograms

B. Objective

The objective of the criteria for GC/MS qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

C. Criteria

1. The relative retention times (RRTs) must be within ±0.06 RRT units of the standard RRT.

2. Mass spectra of the sample compound and a current laboratory-generated standard (i.e., the mass spectrum from the associated calibration standard) must match according to the following criteria:

   a. All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum.

   b. The relative intensities of these ions must agree within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20% and 80%).

D. Evaluation Procedure

1. Verify that the RRT of reported compounds is within ±0.06 RRT units of the standard RRT.

2. Check the sample compound spectra against the laboratory standard spectra to see that it meets the specified criteria.

3. The reviewer should be aware of situations (e.g., high concentration samples preceding low concentration samples) when sample carryover is a possibility and should use judgment to determine if instrument cross-contamination has affected any positive compound identification.

4. Check the chromatogram to verify that peaks are accounted for (i.e., major peaks are either identified as target compounds, TICs, surrogates, or internal standards).

E. Action

1. The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgment. If it is determined that incorrect identifications were made, all such data should be qualified as "not-detected" (flagged "U") or unusable (flagged "R").

2. Professional judgment must be used to qualify the data if it is determined that cross-contamination has occurred.

XI. COMPOUND QUANTITATION AND REPORTING LIMITS

A. Review Items

Form I, Case Narrative, quantitation reports, and chromatograms

B. Objective

The objective is to ensure that the reported quantitation results and reporting limits (RLs) are accurate.

C. Criteria

1. Compound quantitation, as well as the adjustment of the reporting limits, must be calculated according to the correct equation specified in the analytical protocol.

2. Compound RRF must be calculated based on the IS specified in the analytical protocol for that compound. Quantitation must be on the quantitation ion (m/z) specified in the analytical protocol. The

compound quantitation must be based on the RRF from the associated daily standard.

D. Evaluation Procedure

1. Verify that method quantitation limits reported by the laboratory are less than or equal to the reporting limits. If sample dilution is necessary due to elevated target compound concentrations, or if interference related to the sample matrix is observed, method quantitation limits reported by the laboratory may exceed required limits.

2. For all fractions, raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Quantitation lists and chromatograms should be compared to the reported positive sample results and quantitation limits.

3. Verify that the correct IS, quantitation ion, and RRF were used to quantitate the compound. Verify that the same IS, quantitation ion, and RRF are used consistently throughout, in both the calibration as well as the quantitation process.

4. Verify that the reporting limits have been adjusted to reflect all sample dilutions and dry weight factors that are not accounted for by the method.

E. Action

If method quantitation limits reported by the laboratory exceed corresponding project required quantitation limits, and no sample dilutions were necessary or matrix related interference observed, professional judgment should be used to assess the validity of the elevated sample results. The problem should be noted in the quality assurance review.

If any discrepancies are found, the laboratory may be contacted by the designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unsolved, the reviewer must use professional judgment to decide which value is the best value. Under these circumstances, the reviewer may determine if qualification of data is warranted.

XII. FIELD DUPLICATE

A. Review Items

Form I, chromatograms, and quantitation reports

B. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties with collecting identical field samples.

C. Criteria

There are no specific review criteria for field duplicate analyses comparability. Refer to the site QAPP for project-specific requirements for sampling frequency and relative percent differences.

D. Evaluation Procedure

Samples which are field supplicates should be identified. The reviewer should compare the results reported for each sample and duplicate and calculate the relative percent difference (RPD).

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met:

1. A control limit of ±20% (40% for solids) for the RPD shall be used for sample values greater than 5× the reporting limit.

2. A control limit of ± the reporting limit (±2 the reporting limit for solids) shall be used for sample values less than 5 × the reporting limit.

XIII. SYSTEM PERFORMANCE

A. Review Items

For VIII VOA, Form III VOA, and chromatograms

B. Objective

During the period following instrument performance QC checks (e.g., blanks, tuning, calibration), changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

C. Criteria

There is no specific criteria system for performance. Professional judgment should be applied to assess the system performance.

D. Evaluation Procedure

1. Abrupt, discrete shifts in the reconstructed ion chromatogram (RIC) baseline may indicate a change in the instrument's sensitivity or the zero setting. A baseline "shift" could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds, at or near the detection limit, to miss detection. A baseline "rise" could indicate problems such as a change in the instrument zero, a leak, or degradation of the column.

2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   a. High RIC background levels or shifts in absolute retention times of internal standards.

   b. Excessive baseline rise at elevated temperature.

   c. Extraneous peaks.

   d. Loss of resolution.

e. Peak tailing or peak splitting that may result in inaccurate quantitation.

E. Action

Professional judgment must be used to qualify the data if it is determined that system performance has degraded during sample analyses.

XIV. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results and, if available, Quality Assurance Project Plan and Sampling and Analysis Plan.

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability if the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation Procedure

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the Quality Assurance Project Plan, Sampling and Analysis Plan and communication with the data user that concerns the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his assessment of the usability of the data within the given context.

XV. AUTHORITY

This data validation SOP for the analysis for volatile organic compounds by GC/MS has been prepared by Environmental Standards, Inc. for the 3M Corporation Cordova projects. This SOP is not to be used for any other project or by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date: _____

Rock J. Vitale, CPC
Director of Chemistry

STANDARD OPERATING PROCEDURES FOR THE DATA VALIDATION OF SEMIVOLATILE ORGANIC COMPOUNDS BY GC/MS (SW-846, METHOD 8270B)*

I. INTRODUCTION

This method is used to determine a wide range of semivolatile organic compounds including most neutral, acidic, and basic organic compounds which are soluble in methylene chloride. Typically, this method is used to analyze for Target Compound List (TCL), Priority Pollutant List (PPL), and Appendix IX semivolatile compounds. However, this method may also be used for the analysis of additional polynuclear aromatic hydrocarbons, chlorinated hydrocarbons, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, phenols, pesticides, herbicides, insecticides, and PCBs.

This method is applicable for the analysis of extracts from aqueous, soil, and solid waste matrices. Samples are extracted using methylene chloride or other appropriate solvents and concentrated prior to injection into the gas chromatograph/mass spectrometer (GC/MS) for separation and detection of individual compounds. Sample concentrations are determined using internal standard methods. Interferences due to inherent sample matrix contents may affect qualitative and quantitative determinations, and sample extracts may require cleanup prior to analysis. The compounds *alpha*-BHC, *gamma*-BHC, endosulfan I, endosulfan II, and *N*-nitrosodiphenylamine compounds are known to decompose during analysis. Several chlorinated and nitro substituted phenols and anilines are subject to erratic chromatographic behavior.

Method 8270B is subject to laboratory interpretations of analytical and quality control procedures and criteria. In addition, the project-specific Quality Assurance Project Plan (QAPP) may include requirements which differ from those presented in the SOP. Therefore, professional judgment must be used when applying the contents of the SOP to all situations.

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* **See Section XVIII for Authority and Application of this SOP.**

II. TECHNICAL HOLDING TIMES

A. Review Items

Form I SV or equivalent, Chain-of-Custody Records, raw data, sample extraction logs, Case Narrative, and Laboratory Sample Log in documentation

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of extraction and analysis.

C. Criteria

The holding time criteria for semivolatile compounds in cooled (4± 2°C) water samples is seven days from sample collection to extraction and 40 days from sample extraction to analysis. Aqueous samples submitted for semivolatile analysis are typically contained in 1 liter amber glass containers with a Teflon®-lined lid at 4°C.

The holding time criteria for semivolatile compounds in non-aqueous samples (sediments, sludge, soils, and waste) is 14 days from sample collection to extraction and 40 days from sample extraction to analysis. Soil samples submitted for semivolatile analysis are typically contained in 250 ml, widemouth, glass jars with Teflon®-lined lids at 4± 2°C. Waste samples may be submitted in 125 ml jars. Waste samples do not require temperature preservation.

D. Evaluation

Technical holding times are established by comparing the sampling dates on the Chain-of-Custody Records with the dates of extraction and analysis on the Semivolatile Form I's, the sample extraction logs, and the raw data. Verify that the samples were extracted and analyzed within the holding times specified above. Examine the Chain-of-Custody Records and Laboratory Sample Log-in documentation to determine if samples were preserved.

E. Action

If technical holding times were exceeded, document in the quality assurance review that holding times were exceeded from those specified in Chapter 4, Table 4-1 of SW-846, and qualify the sample results according to the following criteria:

1. For aqueous sample extraction:

   a. If extraction of aqueous samples was performed more than seven days but up to 14 days from the date of sample collection, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

   b. If extraction of aqueous samples was performed more than 14 days from the date of collection, flag positive results as estimated (flagged "J") and "not detects" as "R".

2. For aqueous sample analysis:

   a. If aqueous samples were analyzed more than 40 days but up to 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

   b. If aqueous samples were analyzed more than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "R".

3. For solid and waste sample extraction:

   a. If solid samples were extracted more than 14 days but up to 28 days from the date of sample collection, flag positive results "J" and "not-detects" as "UJ".

   b. If extraction of solid samples was performed more than 28 days from the date of collection, flag positive results as estimated (flagged "J") and "not-detects" as "R".

4. For solid and waste sample analysis:

   a. If solid samples were analyzed more than 40 days but less than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

   b. If solid samples were analyzed more than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "R".

5. If aqueous and soil samples were not received at the proper temperature of 4±2°C based on the review of the Chain-of-Custody Records, laboratory sample receipt records and/or Case Narrative the following determination must be made prior to qualification of the data.

   a. If the temperature of the samples was measured by placing the thermometer or probe in between the bottles, air temperature of the cooler or in any free liquid in the cooler due to melting ice, no qualification of data is performed. However, a comment in the validation report should note the temperature recorded, the method of measurement, if ice was present upon laboratory receipt, and that there is no direct impact on the usability of the data.

   b. If the temperature of the samples was based upon the measured temperature of the temperature bottle blank or using an IR gun, the following qualifications are warranted:

      If the temperature of the temperature bottle upon receipt at the laboratory was greater than 6°C but <10°C, a comment will be written in the data validation report addressing the fact that elevated temperatures may lead to a loss of analyte; however, the data reviewer has not considered the data to have been impacted due to the stability and chemical properties (i.e., vapor pressure, boiling point, etc.) of the semivolatile compounds.

      If aqueous soil samples were not received at the proper temperature of 4±2°C, flag positive results as estimated (flagged "J") and "not-detects" as "UJ" if the samples were received at

>10°C but ≤20°C. If received at >20°C, flag positives as estimated (flagged "J") and "not-detects" as "R".

c. Waste samples are not qualified based on temperature issues.

III. GC/MS TUNING

A. Review Items

Form V SV or equivalent, decafluorotriphenylphosphine (DFTPP) mass spectra, and mass listing

B. Objective

GC/MS tuning is performed to ensure mass resolution, identification, and to some degree, sensitivity. These criteria are not sample specific and should be met in all circumstances.

C. Criteria

The analysis of a 50 ng injection (1 µl) of the GC/MS tuning standard solution must be performed at the beginning of each 12-hour period during which samples or standards are analyzed. The GC/MS tuning standard, decafluorotriphenylphosphine (DFTPP) for semivolatile analysis, must meet the ion abundance criteria given below:

DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP)

m/z	ion abundance criteria
51	30-60% of m/z 198
68	less than 2% of m/z 69
70	less than 2% of m/z 69
127	40-60% of m/z 198
197	less than 1% of m/z 198
198	base peak, 100% relative abundance
199	5-9% of m/z 198
275	10-30% of m/z 198
365	greater than 1% of m/z 198

m/z	ion abundance criteria
441	present, but less than m/z 443
442	greater than 40% of m/z 198
443	17-23% of m/z 442

Note: all ion abundances must be normalized to m/z 198, the nominal base peak, even though the ion abundance of m/z 442 may be greater than that of m/z 198. In addition, Method 8270B allows for alternate tuning criteria (i.e., CLP, Method 525, etc.) as long as method performance is not adversely affected.

The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. The GC/MS tuning standard, in addition to DFTPP, should contain 50 ng/µl of 4,4'-DDT, pentachlorophenol, and benzidine. The degradation of 4,4'-DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at responses (area counts) similar to those obtained in the subsequent calibration; peak tailing should not be visible. Many laboratories have interpreted this portion of the GC/MS tuning procedure to be optional.

D. Evaluation

1. Compare the data presented for each tune (Form V SV) with each mass listing submitted to ensure the following:

   a. Form V SV is present and completed for each 12-hour period during which samples were analyzed.

   b. The laboratory has not made transcription errors between the data and the form.

   c. The laboratory has not made calculation errors.

2. Verify from the raw data that the mass alignment is correct and that the mass listing is normalized to m/z 198.

3. Verify that the ion abundance criteria was met. The criteria for m/z 68, 70, 441, and 443 are calculated normalizing to the specified m/z.

4. All instrument conditions must be identical to those used in the sample analysis.

E. Action

1. If the laboratory has made minor transcription errors which do not significantly affect the data, the data reviewer should make the necessary corrections on a copy of the form.

2. If the laboratory has failed to provide the correct forms or has made significant transcription or calculation errors, the reviewer must use professional judgment to assess the data.

3. If mass assignment is in error (such as m/z 199 is indicated as the base peak rather than m/z 198), qualify all associated data as unusable (flagged "R").

4. If ion abundance criteria are not met, professional judgment may be applied to determine to what extent the data may be utilized. The critical ion abundance criteria for DFTPP are the m/z 198/199 and 442/443 ratios. If the laboratory used an alternate method criteria instead, note this as a comment in the quality assurance review and evaluate the tuning against the alternate criteria.

5. Decisions to use analytical data associated with DFTPP tunes not meeting method requirements should be clearly noted in the quality assurance review.

6. If the reviewer has reason to believe that the tuning criteria were achieved using techniques other than those described, additional information on the tuning should be obtained.

7. If the column performance portion of the GC/MS tuning procedure is followed by the laboratory, verify that the percent breakdown of 4,4'-DDT is less than 20%. The following calculation is used:

$$\%\ \text{breakdown of } 4,4' - \text{DDT} = \frac{\text{total DDT degradation peak areas } (\text{DDE} + \text{DDD})}{\text{peak areas } (\text{DDT} + \text{DDE} + \text{DDD})}$$

Review the benzidine and pentachlorophenol peaks on the chromatogram to determine if peak shape and areas or height of the peaks to the subsequent calibration standard are similar. A ratio approach if the standard concentration is different that the 50 ng/µl concentration in the GC/MS tuning standard.

If the 4,4'-DDT exceeds 20% degradation or poor peak shape problems are noted, the data reviewer should note this in the report and use professional judgment to determine the effect on the sample data.

IV. INITIAL CALIBRATION

A. Review Items

Form VI SV or equivalent, quantitation reports, and chromatograms

B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for the semivolatile compounds.

C. Criteria

1. A 1 µl aliquot of each initial calibration standard containing all semivolatile target compounds, internal standards, and surrogate compounds are analyzed at a minimum of five concentrations at the beginning of each analytical sequence, or as necessary if the continuing calibration acceptance criteria are not met. One of the calibration standards should be at a concentration slightly above the laboratory-determined method detection limits. Internal standard compounds are injected into the calibration standards prior to analysis. The initial calibration and any associated samples and blanks must be analyzed within 12 hours of the associated tune.

2. Method criteria state that a minimum <u>average</u> relative response factor (RRF) of 0.050 must be met for the System Performance Check Compounds (SPCCs): *N*-nitroso-di-*n*-propylamine;

hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol. However, for determining data usability, any initial calibration RRF must be greater than or equal 0.050.

3. Method criteria state that the percent relative standard deviation (%RSD) of the relative response factors should be less than 15% for each compound. If the %RSD of any compound is < 15%, then the RRF is assumed to be constant over the calibration range and the average RRF may be used for quantitation. If the %RSD for any compound is greater than 15%, calibration curves of area ratios (area of compound/area of internal standard) versus concentration using first or second order regression are constructed. The use of these regression curves is a recommended alternative to average RRF calibration. As an additional requirement, the %RSD of the relative response factors for each individual Calibration Check Compound (CCC) must be less than 30%. The CCCs are listed in the following table:

Base/Neutral Fraction	Acid Fraction
acenaphthene	4-chloro-3-methylphenol
1,4-dichlorobenzene	2,4-dichlorophenol
hexachlorobutadiene	2-nitrophenol
N-nitrosodiphenylamine	phenol
di-*n*-octylphthalate	pentachlorophenol
fluoranthene	2,4,6-trichlorophenol
benzo(a)pyrene	

If any CCC displays a %RSD > 30%, the laboratory must correct the problem and repeat the initial calibration sequence. However, for determining data usability, the %RSD from the initial calibration must be ≤ 30% for all target compounds.

4. The relative retention times of each compound in each calibration analysis should agree within 0.06 relative retention time units.

D. Evaluation

1. Verify that the correct concentrations of standards were used for the initial calibration and that the low concentration standard is near the method detection limit.

2. Verify that the correct initial calibration was used for all samples.

3. If any sample results were calculated using an initial calibration, verify that the average relative response factor was used for calculating sample results and that the samples were analyzed within 12 hours of the associated tune.

4. Evaluate the initial calibration RRFs for all semivolatile target compounds.

   a. Check and recalculate the RRFs and average RRFs for at least one semivolatile target compound associated with each internal standard; verify that the recalculated value(s) agrees with the laboratory reported value(s). If errors are detected in the calculations, perform a more comprehensive recalculation.

   b. Verify that for all semivolatile target compounds and surrogates, all initial calibration RRFs are greater than or equal to 0.050.

5. Evaluate the %RSD for all semivolatile target compounds.

   a. Check and recalculate the %RSD for one or more semivolatile target compound(s); verify that the recalculated value(s) agrees with the laboratory reported value(s). If errors are detected in the calculations, perform a more comprehensive recalculation.

   b. Verify that all semivolatile target compounds have a %RSD less than or equal to 30%.

6. Evaluate relative retention times for several compounds to verify retention time agreement of 0.06 RRT units.

7. Verify that the internal standard assigned to each analyte for calculation of RRFs is consistent with Table 5 in SW-846 Method 8270B.

E. Action

1. If any semivolatile target compound result has any relative response factors of less than 0.050:

a. Flag positive results for that compound as estimated (flagged "J").

b. Flag "not-detects" for that compound with an "R".

2. If any semivolatile target compound has a %RSD greater than 30%:

a. Flag positive results for that compound as estimated (flagged "J").

b. Flag positive results as estimated (flagged "J") and "not-detects" as "UJ" for any compound with an %RSD of >50%.

c. Flag positive results as estimated (flagged "J") and "not-detects" as "R" for any compound with a %RSD of > 90%.

d. Functional Guidelines (2/94) also suggests eliminating either the high point or the low point to restore the % RSD to ≤ 30%, in which case, only positive results greater than the "new linear range" are flagged "J" or only positive results in the area of nonlinearity are flagged "J".

3. If the assignment of the internal standards does not match Table 5 in SW-846, a non-correctable deficiency should be included in the data validation report. However, for non-SPCC and non-CCC compounds, this issue should have no impact on data quality, as long as the same internal standard is used for that compound for all subsequent continuing calibrations.

V. CONTINUING CALIBRATION

A. Review Items

Form VII or equivalent, quantitation reports, and chromatograms

B. Objective

Continuing calibrations are analyzed to monitor calibration and compound response drift and checks satisfactory performance of the instrument on a day-to-day basis.

C. Criteria

1. A mid concentration continuing calibration standard containing target compounds and surrogate compounds is analyzed at the beginning of each 12-hour analysis period following the analysis of the tune and prior to the analysis of the method blank and samples.

2. Method criteria state that a minimum daily relative response factor (RRF) of 0.050 must be met for the System Performance Check Compounds (SPCCs): 2,4-dinitrophenol, *N*-nitroso-di-*n*-propylamine, hexachlorocyclopentadiene, and 4-nitrophenol. However determining data usability, any continuing calibration RRF must be greater than or equal 0.050.

3. Method criteria state that percent difference (percent drift) should be less than 20% for each CCC. Percent drift is calculated using the following equation:

$$\%Drift = ([C_I - C_c] / C_I) * 100$$

where:
C_I = Calibration check compound standard concentration.
C_c = Measured concentration of continuing calibration CCC.
If the %Drift of each CCC is <20%, then the initial calibration is assumed to be valid. The CCCs are listed in the following table:

Base/Neutral Fraction	Acid Fraction
acenaphthene	4-chloro-3-methylphenol
1,4-dichlorobenzene	2,4-dichlorophenol
hexachlorobutadiene	2-nitrophenol
N-Nitrosodiphenylamine	phenol
di-*n*-octylphthalate	pentachlorophenol
fluoranthene	2,4,6-trichlorophenol
benzo (a) pyrene	

It should be noted that if these CCCs are not target compounds for the specific analysis, then all target compounds are considered CCCs for the analysis.

If any SPCC RRF is <0.050 or CCC %Drift is $>20\%$, the laboratory must correct the problem. If no source of the problem can be determined, the initial calibration sequence must be repeated.

It should be noted that the percent drift is equivalent to the percent difference between response factors as calculated per CLP protocols.

Compare the internal standard retention times and areas using the Form VIII - SV, or equivalent forms, for the following criteria:

The retention time for any internal standard in the continuing calibration must be within 30 seconds of the internal standard retention times from the previous initial or continuing calibration.

The internal standard area for any of the internal standards must be within -50% to +100% of the internal standard areas from the previous initial or continuing calibration

If these criteria are exceeded, the laboratory must inspect for malfunctions, and corrections must be made. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

D. Evaluation

1. Verify that the continuing calibration was run at the required frequency and that the continuing calibration was compared to the correct initial calibration.

2. Evaluate the continuing calibration RRF for all semivolatile target compounds.

   a. Check and recalculate the RRF for at least one semivolatile target compound associated with each internal standard; verify that the recalculated value(s) agrees with the laboratory reported value(s). If errors are detected in the calculation of the RRFs, perform a more comprehensive recalculation.

   b. Verify that the RRF is >0.050 for all semivolatile compounds.

3. Evaluate the %Drift from the initial calibration for each continuing calibration.

   a. Check and recalculate the %Drift for at least one semivolatile target compound associated with each internal standard; verify that the recalculated value(s) agrees with the laboratory reported value(s). If errors are detected in the calculation of the RRFs, perform a more comprehensive recalculation.

   b. Verify that the %Drift is $\leq 20\%$ for all semivolatile compounds.

4. Verify that the continuing calibration internal standard area counts and retention times are acceptable when compared to the previous, initial, or continuing calibration internal standard responses.

E. Action

1. If any semivolatile target compound result has a relative response factor less than 0.50:

   a. Flag positive results for that compound as estimated (flagged "J").

b. Flag "not-detects" for that compound with an "R".

2. If any semivolatile target compound has a %Drift greater than greater than 20%:

   a. Flag positive results for that compound as estimated (flagged "J").

   b. "Not-detects" for that compound may be qualified using professional judgment. In particular, if a high % Drift is due to a decrease in instrument sensitivity, qualify the associated "not-detected" result as estimated ("UJ"). If a high % Drift is due to an increase in instrument sensitivity, qualify the "not-detected" results as estimated ("UJ"), but note in the quality assurance review that because of the increase in instrument sensitivity, the reporting limit may be acceptable as reported by the laboratory.

3. If a % Drift greater than 90% is observed for a compound, qualify all positive results for the compound in the associated samples as estimated ("J") and all "not-detected" results in the associated samples as unreliable ("R"), whether or not the high % Drift is in the direction of increasing or decreasing sensitivity.

4. Data is not necessarily qualified if the continuing calibration standard does not display acceptable internal standard responses (in regard to area counts and retention times) when compared to the previous initial or continuing calibration standards. For instance, if a continuing calibration displayed poor area counts for one or more internal standards, but the associated samples displayed acceptable internal standard area counts when compared to the associated initial calibration, data should not be qualified because the sample quantitation is based on the average relative response factors from the initial calibration. However, if the continuing calibration and associated samples display unacceptable internal standard responses, data for the samples should be qualified, even though the internal standard responses for the samples could be acceptable when compared to the associated continuing calibration. In any case, whenever a continuing calibration displays unacceptable internal standard area counts or retention times, consult the Project Manager or a senior chemist for guidance.

VI. METHOD AND FIELD BLANK

A. Review Items

Blank Form I SV or equivalent, Form IV SV or equivalent, chromatograms, extraction logs, and quantitation reports

B. Objective:

The assessment of blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting other data.

C. Criteria

1. No method-specific requirements concerning acceptable contaminant concentrations are listed in the method.

2. A method blank analysis must be performed each time a set of samples is extracted or whenever there is a change in reagents. A blank should be carried through all stages of sample preparation and analysis.

3. The frequency of field blanks is determined during the sampling event. A minimum of one field blank is suggested for each sample delivery group. Refer to the QAPP for project-specific criteria for the sampling frequency and acceptability of field blanks.

D. Evaluation

1. Review the results of all associated blanks on the forms and raw data (chromatograms and quantitation reports) to evaluate the presence of target and non-target compounds in the blanks. Tabulate the method blank and field results on the Environmental Standard Blank Analysis Results Forms. Convert method blank results reported in µg/L to µg/Kg for qualification of soil samples.

2. Verify that a method blank analysis has been reported for each extraction batch.

E. Action

If the appropriate blanks were not analyzed with the frequency described in Criteria 2 and 3 in Section VI.C, then the reviewer should use professional judgment to determine if the associated sample data should be qualified. If no field blanks are associated with the samples, a comment indicating that potential contamination due to field sampling can not be evaluated must be included in the quality assurance review.

Action in the case of unsuitable blank results depends on the origin and circumstances of the blank.

Positive sample results are not qualified for associated blank contamination unless the concentration of the compound in the sample is less than or equal to 10 times (10×) the amount in any blank for the common semivolatile laboratory contaminants (i.e., phthalates) or five times (5×) the amount for other semivolatile target compounds. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated method blank having the highest concentration for a contaminant. Qualification using multiple field blanks should be based upon comparison and association with the samples using the sample collection date. The project sample results must not be corrected by subtracting any blank value. When comparing blank concentrations to sample concentrations, the same weights, volumes, dilutions, and dry weight correction factors must be considered when comparing blank results to project samples. It is often quicker and more convenient to compare instrument levels when considering blank contamination.

Specific actions are as follows:

1. If a semivolatile compound is found in a blank but not found in the sample, no action is taken.

2. If the sample result is greater than the reporting limit (RL), but less than the required amount (5× or 10×) from the blank result, the sample results are qualified as not detected ("U").

3. If the sample result is positive, but less than the RL, and less than the required amount (5× or 10×) from the blank result, the result is raised to the RL and is flagged as not detected ("U").

4. If the sample result is greater than the required amount (5× or 10×) from the blank result, the sample results are not qualified.

5. If gross contamination exists (i.e., saturated peaks by GC/MS), all affected compounds in the associated samples should be qualified as "R" due to interferences.

6. The same consideration given to the target compounds should also be given to tentatively identified compounds (TICs) that are found in both the sample and associated blank(s). However, the 5× and 10× rules do not apply and compounds found in both the blank and samples should be flagged "R" on the form I-TICs.

7. If low-level phthalates are not qualified based on blank contamination, a qualifier indicating phthalates are common laboratory contaminants should be included in the data validation report and urge caution when using the sample result.

VII. SURROGATE RECOVERY

A. Review Items

Form II SV, quantitation reports, and chromatograms

B. Objective

Laboratory performance on individual samples is established by means of spiking activities. All samples are spiked with surrogate compounds prior to sample purging. The evaluation of the results of these surrogate compounds is not necessarily straightforward. The sample matrix itself may interfere with the analysis due to such factors as high analyte concentration. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present unique or unusual problems, the evaluation and review of data based on

specific sample results is frequently subjective and demands analytical experience and professional judgment.

C. Criteria

1. Surrogate compounds (three acid compounds and three base/neutral compounds) are added to all samples and blanks to measure their recovery in environmental samples and blank matrices.

   At a minimum, the laboratory should update surrogate recovery limits on a matrix-by-matrix basis. Based on a minimum population of 30 samples, an average percent recovery and standard deviation of the percent recoveries are calculated by the laboratory. For each matrix, an upper and lower control limit for method performance for each surrogate standard is calculated using ± 3 times the calculated standard deviation. Once the laboratory established limits are calculated, they are compared to the method-specified control limits as listed below. (The laboratory established surrogate recovery limits must fall within the limits listed below.)

2. Recoveries for surrogate compounds in semivolatile samples and blanks must be within the limits specified below. If one or more surrogate recoveries in a sample are outside these limits, the laboratory must either reextract and reanalyze the sample or sampling quality and all associated data as estimated.

Surrogate Compound Criteria

Surrogate	Water %R
nitrobenzene-d_5	36-148%
2-fluorobiphenyl	38-106%
terphenyl-d_{14}	10-169%
phenol-d_6	15-126%
2-fluorophenol	17-106%
2,4,6-tribromophenol	13-145%

D. Evaluation

1. Check raw data (i.e., chromatograms and quantitation reports) to verify the recoveries on the surrogate recovery Form II SV. Check for any calculation or transcription errors.

2. The following should be determined from the Surrogate Recovery Form(s):

   a. If any surrogate compounds in the semivolatile fraction are out of specification, there should be a reanalysis to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies. However, Method 8270B does not require reanalysis of samples not meeting surrogate recovery criteria; the laboratory has the option of simply qualifying the data as "estimated concentration."

      Note: when there are unacceptable surrogate compound recoveries followed by successful reanalyses, the laboratory may report only the results for the successful run.

   b. Verify that no blanks have surrogate compounds outside the criteria.

E. Action

Data are qualified based on surrogate compound results if the recovery of any semivolatile surrogate compound is out of specification. For surrogate compound recoveries out of specification, the following approaches are suggested:

1. If two or more surrogates in either semivolatile fraction (acid or base/neutral) have a recovery greater than the upper acceptance limit:

   a. Positive semivolatile target compounds for that fraction are qualified as estimated (flagged "J").

   b. Results for "not-detected" semivolatile target compounds for that fraction should not be qualified.

2. If two or more surrogates in either semivolatile fraction have a recovery greater than or equal to 10% but less than the lower acceptance limit:

   a. Positive semivolatile target compounds for that fraction are qualified as estimated (flagged "J").

   b. Results for "not-detected" semivolatile target compounds for that fraction should be qualified "UJ".

3. If any surrogate compound in either semivolatile fraction has a recovery less than 10%:

   a. Positive semivolatile target compounds for that fraction are qualified as estimated (flagged "J").

   b. Results for "not-detected" semivolatile target compounds for that fraction should be qualified "R".

4. If a laboratory reports surrogate recovery ranges which are larger than those specified above, qualify sample data based on the recovery ranges specified above and note the large recovery ranges in the quality assurance review.

5. In the special case of a blank or laboratory control sample with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. Professional judgment should be used to determine if the surrogate outside criteria is an isolated occurrence or a systemic problem.

VIII. MATRIX SPIKE/MATRIX SPIKE DUPLICATES

A. Review Items

Form III SV or equivalent, chromatograms, and quantitation reports

B. Objective

Data for matrix spike/matrix spike duplicates (MS/MSDs) are generated to determine long-term precision and accuracy of the analytical method on various matrices and demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone are not used to evaluate the precision and accuracy of other samples.

C. Criteria

1. MS samples are analyzed at a frequency of one MS per 20 samples of a similar matrix.

2. Many laboratories also perform a MSD analysis as an additional laboratory QC requirement, or as project specific requirements at a frequency the same as for the matrix spike.

3. Method 8270B provides three methods for determining the spike concentration. However, two of these methods require that the unspiked sample be analyzed prior to spiking and extracting the matrix spike sample. The analysis of the unspiked sample determines the background concentrations prior to spiking so appropriate spiking levels can be added to the matrix spike sample.

   As stated in the method, if it is impractical to determine background levels before spiking, the spike concentration should be at the regulatory concentration limit, or the larger of either five times higher than the expected background concentration, or 100 µg/L. For other matrices, the recommended spiking concentration is 20 times the ERL.

4. Environmental Standards interprets Method 8270B to indicate that the laboratory should perform a matrix spike analysis to include all target analytes. However, the method provides recovery limits for a specific number of compounds. Spike recoveries should be within the limits found in Table 6 of Method 8270B.

5. Laboratories may opt to perform a MS/MSD analysis using a reduced list of analytes or the Contract Laboratory spiking amounts and criteria. These criteria are provided below.

6. If the laboratory spiked the MS/MSD sample with the CLP spike compounds, relative percent differences (RPDs) between MS and MSD recoveries must be within the advisory limits provided on Form III SV as listed below:

MS/MSD CRITERIA

	Aqueous	
Compound	%R	RPD
phenol	10-107%	35%
2-chlorophenol	10-134%	28%
1,4-dichlorobenzene	33-90%	37%
N-nitroso-di-*n*-propylamine	10-230%	30%
1,2,4-trichlorobenzene	40-133%	35%
4-chloro-3-methylphenol	21-120%	49%
acenaphthene	45-122%	28%
4-nitrophenol	10-144%	100%
2,4-dinitrotoluene	37-124%	34%
pentachlorophenol	10-122%	71%
pyrene	15-124%	45%

D. Evaluation

1. Verify that MS or MS/MSD samples were analyzed at the required frequency and that results are provided for each sample matrix.

2. Inspect results for the MS or MS/MSD recovery on Form III SV and verify that the results for recovery and RPD are within the limits on Table 6 in Method 8270B.

3. Verify transcriptions from raw data and verify calculations.

4. Compare %RSD results of nonspiked compounds between the unspiked result, MS, and MSD samples.

E. Action

1. No action is taken on MS or MS/MSD data alone. However, using informed professional judgment, the data reviewer may use the MS or

MS/MSD results in conjunction with the other QC criteria and determine the need for some qualification of the data.

2. Although the laboratory is required to use the MS recovery ranges listed in Table 6 as method criteria, Environmental Standards will determine data usability using the following criteria. Note that data will not be qualified if the indigenous level of a compound in the unspiked sample is greater than four times the spiking level for the compound.

   a. If any matrix spike compound has a recovery of $<10\%$, positive results for that compound in the unspiked sample are qualified as estimated (flagged "J") and "not-detected" results should be qualified "R".

   b. If any matrix spike compound has a recovery between 11% and 49%, positive results for that compound in the unspiked sample are qualified as estimated (flagged "J") and "not-detected" results should be qualified "UJ".

   c. If any matrix spike compound has a recovery between 50% and 135%, the results are acceptable and do not require qualification.

   d. If any matrix spike compound has a recovery $>135\%$, positive results for that compound in the unspiked sample are qualified as estimated (flagged "J").

3. If the laboratory performs an MS/MSD analysis, qualify data based on the RPDs between the MS and MSD concentrations in the following manner:

   a. If the RPD for a compound exceeds 30% for an aqueous MS/MSD analysis or 50% for a solid sample MS/MSD analysis, flag the positive result for that compound in the unspiked sample as estimated ("J").

   b. "Not-detected" results are not qualified due to high RPDs in the MS/MSD analysis.

4. In the instance where the laboratory has adopted the Contract Laboratory Program spiking list and acceptance criteria, note the issue in the quality assurance review. In addition, data usability will be determined using the following criteria. As stated above, if the indigenous concentration of a compound in the unspiked sample is greater than four times the spiking concentration, data will not be qualified based on the MS/MSD recoveries for that compound.

   a. If the recovery of a matrix spike compound in the semivolatile MS and/or MSD has a recovery greater than the upper acceptance limit, positive results for that compound in the unspiked sample should be considered estimated (flagged "J").

   b. If the recovery of a matrix spike compound in the semivolatile MS and/or MSD has a recovery less than the lower acceptance limit and $>10\%$, the positive result for that compound in the unspiked sample should be considered estimated (flagged "J") and the "not-detected" result should be flagged "UJ".

   c. If the recovery of a matrix spike compound in the semivolatile MS and/or MSD has a recovery less than 10%, "not-detected" results for that compound in the unspiked sample should be flagged "R".

   d. If MS/MSD pairs exceed the specified RPD, positive results for that compound in the unspiked sample should be considered estimated (flagged "J").

IX. BLANK SPIKES/LABORATORY CONTROL SAMPLES

A. Review Items

Form III or equivalent for LCS results, quantitation reports, and chromatograms

B. Objective

To establish the ability to generate acceptable accuracy and precision for each target analyte.

C. Criteria

1. If any analyte in the matrix spike sample fails the acceptance criteria for recovery, a QC reference sample (LCS) containing each analyte that failed the MS recovery must be prepared and analyzed. If all target compounds meet acceptance criteria, an LCS is not required.

2. The frequency for the required analysis of the LCS is dependent upon the number of analytes analyzed, the complexity of the sample matrix, and laboratory performance. If a large number of analytes are analyzed, the probability that a LCS would be required is high. Therefore, many laboratories will prepare, extract, and analyze LCS for all analytes with each SDG.

3. LCS recoveries should be within the limits provided in the table below.

Compound	Recovery Criteria
1,2,4-trichlorobenzene	39-136%
acenaphthene	48-113%
2,4-dinitrotoluene	37-131%
pyrene	39-159%
N-nitrosodi-*n*-propylamine	31-113%
1,4-dichlorobenzene	37-92%
pentachlorophenol	10-113%
phenol	12-116%
2-chlorophenol	35-111%
4-chloro-3-methylphenol	30-117%
4-nitrophenol	10-128%

D. Evaluation

1. Verify that LCS was analyzed for those analytes which displayed recoveries outside the specified recovery ranges for the MS analyzed.

2. Inspect results for the LCS recoveries and verify that the results for the recoveries are within the limit on the table in Section IX.C, above.

3. Verify transcriptions from raw data and verify correct calculations of LCS results.

E. Action

1. If any LCS compound has a recovery of $<10\%$, positive results for that compound in all associated samples are qualified as estimated (flagged "J") and "not-detected" results should be qualified "R".

2. If any LCS compound has a recovery between 11% and the lower limit, positive results for that compound in all associated samples are qualified as estimated (flagged "J") and "not-detected" results should be qualified "UJ".

3. If any LCS compound has a recovery greater than the upper limit, positive results for that compound in all associated samples are qualified as estimated (flagged "J").

X. INTERNAL STANDARDS

A. Review Items

Form VIII SV or equivalent, quantitation reports, and chromatograms

B. Objective

Internal Standards (IS) performance criteria ensure that GC/MS sensitivity and response are stable during every analysis.

C. Criteria

1. The recommended internal standards are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. The concentration of the internal standard in the extract should be 40 ng/µl for each internal standard.

2. Internal standard area counts from each sample, blank, or QC sample should not vary by more than a factor of two (-50% to +100%) from

the associated calibration standard. It should be noted that this is not a requirement of the method.

3. Internal standard area counts from the continuing calibration must not vary by more than a factor of two (-50% to +100%) from the previous initial or continuing calibration.

4. The retention time of the internal standard from each sample, blank, or QC sample should not vary more than ±30 seconds from the associated calibration standard. It should be noted that this item is not a requirement of the method.

5. The retention time of the internal standards from the continuing calibration must not vary more than ±30 seconds from the previous initial or continuing calibration.

D. Evaluation

1. Check raw data (e.g., chromatograms and quantitation lists) to verify the internal standard retention times and areas reported on the Internal Standard Area Summary Forms (Form VIII SV).

2. Verify that all retention times and internal standard areas are within criteria.

3. If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations should include:

   a. Magnitude and direction of the internal standard area shift.

   b. Magnitude and direction of the internal standard retention time shift.

   c. Technical holding times.

   d. Comparison of the values of the target compounds reported in each fraction.

e. Other quality control (QC) data results.

4. Verify stability of areas and retention times of the internal standards. If criteria are not met, the laboratory may reanalyze the samples, but this is not a requirement of SW-846 Method 8270B.

E. Action

1. If an internal standard area count for a sample or blank is outside -50% or +100% of the area for the associated standard:

   a. Positive results for compounds quantitated using that IS should be qualified as estimated (flagged "J").

   b. "Not-detected" results reported using an IS area count less than -50% or greater than +100% are reported as the associated reporting limit and qualified "UJ".

   c. If extremely low area counts are reported, or if performance exhibits a major abrupt drop-off, then a severe loss of sensitivity is indicated. "Not-detected" target compounds should then be qualified as unusable (flagged "R").

2. If an internal standard retention time varies by more than 30 seconds, the chromatographic profile for that sample must be examined to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection of that data for that sample fraction. If the mass spectral criteria are met, positive results should not need to be qualified as "R".

3. If one or more internal standards for a sample, blank, or QC sample displayed unacceptable retention times or area counts and the laboratory did not reanalyze the sample extract, include a comment concerning this issue in the quality assurance review.

XI. TARGET COMPOUND IDENTIFICATION

A. Review Items

Form I SV or equivalent, quantitation report, mass spectra, and chromatograms

B. Objective

The objective of the criteria for GC/MS qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

C. Criteria

1. The relative retention times (RRTs) must be within ±0.06 RRT units of the standard RRT.

2. Mass spectra of the sample compound and a current laboratory-generated standard (i.e., the mass spectrum from the associated calibration standard) must match according to the following criteria:

   a. The characteristic ions from the reference mass spectrum (defined to be the three ions of greatest relative intensity or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum) must maximize in the same scan or within one scan of each other.

   b. The relative intensities of these characteristic ions must agree within ±30% between the standard and sample spectra. (Example: for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20% and 80%.)

   c. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between the two isomer peaks

is less than 25% of the sum of the two peak heights; otherwise, structural isomers are identified as isomeric pairs.

3. In general, GC/MS analyses are not capable of distinguishing semivolatile compounds diphenylamine and *N*-nitrosodiphenylamine. If a positive result is reported for either of these compounds, examine the raw data to determine if the system and analysis are capable of distinguishing between the two compounds.

D. Evaluation

1. Check that the RRT of reported compounds is within ±0.06 RRT units of the standard RRT.

2. Check the sample compound spectra against the laboratory standard spectra to see that it meets the specified criteria.

3. The reviewer should be aware of situations (e.g., high concentration samples preceding low concentration samples) when sample carryover is a possibility, and should use judgment to determine if instrument cross-contamination has affected any positive compound identification.

4. Check the chromatogram to verify that peaks are accounted for (i.e., major peaks are either identified as target compounds, TICs, surrogates, or internal standards). In addition, check for possible coeluting isomers (it is helpful to check the associated continuing calibration standard also) and for reported positive results for *N*-nitrosodiphenylamine and/or diphenylamine.

E. Action

1. The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgment. If it is determined that incorrect identifications were made, all such data should be qualified as "not-detected" (flagged "U") or unusable (flagged "R"). A copy of the mass spectra must be placed in the support documentation section of the report to substantiate the qualifier.

2. Professional judgment must be used to qualify the data if it is determined that cross-contamination has occurred.

3. If structural isomers are observed to coelute on the GC column used for analysis, identify the coeluting isomers in the quality assurance review. If practical to do so, change the data tables to reflect the fact that the isomers should be considered one analyte.

4. If a positive result is reported for *N*-nitrosodiphenylamine or diphenylamine and the laboratory GC/MS system cannot distinguish between the compounds, include a comment to this effect in the quality assurance review.

XII. COMPOUND QUANTITATION AND REPORTED RLs

A. Review Items

Form I SV or equivalent, Case Narrative, quantitation reports, and chromatograms

B. Objective

The objective is to ensure that reported quantitation results and contract-required reporting limits (RLs) are accurate.

C. Criteria

1. When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion.

2. If the %RSD of a compound's relative response factor is 15% or less, then the concentration in the extract may be determined using the average relative response factor (RRF) from initial calibration date and the following equation:

$$C_{ex}(mg/L) = \frac{(A_x \times C_{is})}{(A_{is} \times \overline{RRF})}$$

where: C_{ex} - concentration of the compound in the extract
A_x - area of the quantitation ion of the compound of interest
A_{is} - area of the quantitation ion of the associated internal standard
C_{is} - concentration of the internal standard
$\overline{RRF}$ - average relative response factor from associated initial calibration

3. Alternatively, the regression line fitted to the initial calibration may be used for determination of the extract concentration.

4. Compute the concentration of the analyte in the sample using the following equations:

   a. The concentration of the analyte in the liquid phase of the sample is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid } (\mu g/L) = \frac{(C_{ex} \times V_{ex}) \times D}{V_o}$$

   where:
   V_{ex} = extract volume, in mL
   V_o = volume of liquid extracted, in L
   D = dilution factor

   b. The concentration of the analyte in the solid phase of the sample is calculated using the concentration of the pollutant in the extract and the weight of the solids, as follows:

$$\text{Concentration in solid } (\mu g/kg) = \frac{(C_{ex} \times V_{ex}) \times D}{W_s \times S}$$

where:

V_{ex} = extract volume, in mL
W_s = sample weight, in kg
S = percent solids of sample, expressed as a fractional number (e.g., 75% solids would be 0.75)
D = dilution factor

Note: Method 8270B does not specify dry weight correction of results; however, this is normally done by the laboratory and is required in most QAPPs.

D. Evaluation

1. Verify that method reporting limits reported by the laboratory are less than or equal to the RLs. If sample dilution is necessary due to elevated target compound concentrations, or if interference related to the sample matrix is observed, method reporting limits reported by the laboratory may exceed required limits.

2. For all fractions, raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Quantitation lists and chromatograms should be compared to the reported positive sample results and reporting limits.

3. Verify that the correct internal standard, quantitation ion, and RRF are used to quantitate the compound. Verify that the same internal standard, quantitation ion, and RRF are used consistently throughout, in both the calibration and the quantitation process.

4. Verify that the RLs have been adjusted to reflect all sample dilutions and dry-weight factors that are not accounted for by the method.

E. Action

If method reporting limits reported by the laboratory exceed corresponding project required reporting limits and no sample dilutions were necessary, or matrix related interference observed, professional judgment should be used to

assess the validity of the elevated sample results. The problem should be noted in the quality assurance review.

If any discrepancies are found, the laboratory may be contacted by the designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unsolved, the reviewer must use professional judgment to decide which value is the best value. Under these circumstances, the reviewer may determine if qualification of data is warranted.

XIII. TENTATIVELY IDENTIFIED COMPOUNDS (If requested for analysis)

A. Review Items

Form I SV or equivalent, chromatograms, library search printouts, and spectra for the three TIC candidates

B. Objective

Chromatographic peaks in the semivolatile fraction that are not target analytes, surrogate compounds, or internal standard compounds are potential TICs. TICs must be qualitatively identified by a National Institute of Standards and Technology (NIST) mass spectral library search and the identifications must be assessed by the data reviewer.

C. Criteria

For each sample, the laboratory must (if requested) conduct a mass spectral search of the NIST library and report the possible identity for the 20 to 30 largest semivolatile fraction peaks which are not surrogate compounds, internal standard compounds, or target compounds, but which have areas or heights greater than 10% of the area of height of the nearest internal standard. TIC results are reported for each sample on the Form I SV - TIC. Refer to the QAPP for specific requirements for TIC searches.

Note: CLP does not allow the laboratory to report any target compounds as TICs which are properly reported in another fraction. Most laboratories either follow this protocol for TICs or do not count these (as well as aldol condensates and laboratory artifacts) in the 20 to 30 TIC searches.

D. Evaluation

1. Guidelines for tentative identification are as follows:

   a. Major ions (greater than 10% relative intensity) in the reference spectrum should be present in the sample spectrum.

   b. The relative intensities of the major ions should agree within ±20% between the sample and the reference spectra.

   c. Molecular ions present in the reference spectrum should be present in the sample spectrum.

   d. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination, interference, or coalition of additional TICs or target compounds.

   e. When the above criteria are not met, but in the technical judgment of the data reviewer or mass spectral interpretation specialist, the identification is correct, the data reviewer may report the identification.

   f. In the data reviewer's judgment, if the identification is uncertain or there are extenuating factors affecting compound identifications, the TIC result may be reported as "unknown."

2. Check the raw data to verify that the laboratory has generated a library search for all required peaks in the chromatograms for samples and blanks.

3. Blank chromatograms should be examined to verify that TIC peaks present in samples are not found in blanks. When a low-level, non-target compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which are less than 10% of the internal standard height, but present in the blank chromatogram at a similar relative retention time.

4. All mass spectra for every sample and blank must be examined.

5. Since TIC library searches often yield several candidate compounds having a close matching score, all reasonable choices must be considered.

6. The reviewer should be aware of common laboratory artifacts/contaminants and their sources (e.g., aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.

   a. Common laboratory contaminants: CO_2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2,-trifluoroethane, or fluorotrichloromethane), and phthalates at levels less than 100 µg/L or 4000 µg/Kg.

   b. Solvent preservatives such as cyclohexene, which is a methylene chloride preservative, may be present. Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.

   c. Aldol condensation reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

7. Occasionally, a target compound may be identified in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list. If the total area quantitation method was used, the reviewer should request that the laboratory recalculate the result using the proper quantitation ion. In addition, the reviewer should evaluate other sample chromatograms and check library reference retention times on quantitation lists to determine whether the false negative result is an isolated occurrence or whether additional data may be affected.

8. Target compounds could be identified in more than one fraction. Verify that quantitation is made from the proper fraction.

9. Library searches should not be performed on internal standards of surrogate compounds.

10. TIC concentration should be estimated assuming a RRF of 1.0 and quantitated from the internal standard nearest in retention time (free of interference) to the TIC.

E. Action

1. All TIC results identified with a specific compound name should be qualified "NJ" (tentatively identified), with approximate sample concentrations. All other TICs (not identified as laboratory artifacts or blank contamination) should be flagged "J" as estimated concentrations.

2. General actions related to the review of TIC results are as follows:

   a. If it is determined that a tentative identification of a non-target compound is not acceptable, the tentative identification should be changed to "unknown" or an appropriate identification.

   b. If all contractually required peaks were not library searched and quantitated, the data reviewer should request these data from the laboratory.

3. When a compound is found in any blank, or is a suspected artifact or common laboratory contaminant, the result may be qualified as "R".

4. In deciding whether a library search result for a TIC represents a reasonable identification, professional judgment must be exercised. If there is more than one possible match, the result may be reported as "either compound X or compound Y." If there is a lack of isomer specificity, the TIC result may be changed to a non-specific isomer result (e.g., 1,3,5-trimethylbenzene may be changed to trimethylbenzene isomer) or to a compound class (e.g., 2-methyl-3-ethylbenzene to substituted aromatic compound).

5. The reviewer may elect to report all similar compounds as a total (e.g., all alkanes may be summarized and reported as total hydrocarbons).

6. Other case factors may influence TIC judgments. If a TIC match is poor but other samples have a TIC with a good library match, similar relative retention time, and the same ions, identification information may be inferred from the other sample TIC results.

7. Physical constants, such as boiling point, may be factored into professional judgment of TIC results.

XIV. LABORATORY DUPLICATES

A. Review Items

Laboratory Duplicate Summary Form, chromatograms, and quantitation reports

B. Objective

Laboratory duplicate (or replicate as stated in Method 8270B) samples are analyzed as an indication of overall laboratory precision. It is expected that soil duplicate results will have a greater variance than water matrices.

C. Criteria

1. The laboratory must analyze a duplicate (replicate) for each analytical batch to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of matrix spiked samples.

2. There are no specific method criteria established for laboratory duplicate comparability.

D. Evaluation

The reviewer should compare the results reported for each sample and duplicate and recalculate several of the relative percent differences (RPDs).

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met:

1. A control limit of ±20% (40% for solids) for the RPD shall be used for sample values greater than 5 × the RL.

2. A control limit of ± 1× the RL (±2 × the RL for solids) shall be used if at least one value is less than 5 × the RL.

If the laboratory did not perform an MSD or a laboratory duplicate analysis, include a deficiency to this effect in the quality assurance review.

XV. FIELD DUPLICATE

A. Review Items

Form I SVs, chromatograms, and quantitation reports

B. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples. Refer to the QAPP for project-specific requirements for field duplicates.

C. Criteria

There are no specific method review criteria for field duplicate analyses comparability.

D. Evaluation

Samples which are field duplicates should be identified. The reviewer should compare the results reported for each sample and duplicate and calculate the relative percent difference (RPD) using Environmental Standards' computer generated forms.

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met:

1. A control limit of ±20% (40% for solids) for the RPD shall be used for sample values greater than 5 × the RL.

2. A control limit of ± the RL (±2 × the RL for solids) shall be used if at least one value is less than 5 × the RL.

If a field duplicate pair was not submitted with the project samples, include a comment to this effect in the quality assurance review.

XVI. SYSTEM PERFORMANCE

A. Review Items

Form VIII SV, Form III SV, and chromatograms

B. Objective

During the period following instrument performance QC checks (e.g., blanks, tuning, etc.), calibration changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

C. Criteria

There is no specific criteria for system performance. Professional judgment should be applied to assess the system performance.

D. Evaluation

1. Abrupt, discrete shifts in the reconstructed ion chromatogram (RIC) baseline may indicate a change in the instrument's sensitivity or the zero setting. A baseline "shift" could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds, at or near the detection limit, to miss detection. A baseline "rise" could indicate problems such as a change in the instrument zero, a leak or degradation of the column.

2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   a. High RIC background levels or shifts in absolute retention times of internal standards.

   b. Excessive baseline rise at elevated temperatures.

   c. Extraneous peaks.

   d. Loss of resolution.

   e. Peak tailing or peak splitting that may result in inaccurate quantitation.

E. Action

Professional judgment must be used to qualify the data if it is determined that system performance has degraded during sample analyses.

XVII. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results and, if available, Quality Assurance Project Plan, and Sampling and Analysis Plan

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data-user in avoiding inappropriate use of the data. Review all available information, including the Quality Assurance Project Plan, Sampling and Analysis Plan, and communication with the data-user that concerns the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and

required quality of the data are available, the reviewer should include his assessment of the usability of the data within the given context.

XVIII. AUTHORITY

This data validation SOP for the analysis for semivolatile organic compounds by GC/MS has been prepared for use on the 3M Corporation Cordova projects by Environmental Standards, Inc. This SOP is not to be used for any other project or by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP Approved by:

_____ Date: _____

Rock J. Vitale, CPC
Director of Chemistry

STANDARD OPERATING PROCEDURES FOR DATA VALIDATION

OF CHLORINATED HERBICIDES BY GC/ECD (METHOD 8151)*

I. INTRODUCTION

This method is for the analysis of chlorinated acid herbicides in aqueous, solid, and waste samples. Samples are spiked with two surrogate compounds (typically 2,4-DCAA and 2,4-DB), acidified, and extracted, based on the matrix, using diethyl ether for aqueous samples and a mixture of acetone and methylene chloride for solid and waste samples. The extract may then undergo a hydrolysis step to convert herbicide esters into the acid derivatives prior to sample analysis if the acid equivalents are desired. If herbicide esters are desired, the hydrolysis conditions for the esters in aqueous and solid extracts are described in Method 8151. The extract is dried and concentrated, and subsequently analyzed by gas chromatography (GC). The compounds of interest are detected through the use of an electron capture detector (ECD).

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the condition of the analysis by analyzing reagent blanks.

Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or water to check for cross contamination.

Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled. Organic acids, especially chlorinated acids, cause the most direct interference with the determination by methylation. Phenols, including chlorophenols, may also interfere with this procedure. The determination using pentafluorobenzylation is more sensitive and therefore, more prone to interferences from the presence of organic acids or phenols than by methylation. Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated

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* **See Section XVI for Authority and Application of this SOP.**

hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis. However, hydrolysis may result in the loss of dinoseb and the formation of aldol condensation products if any residual acetone remains from the extraction of solids. Herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware must be acid-rinsed and then rinsed to constant pH with organic-free reagent water. Sodium sulfate must be acidified.

If peak detection and identification are prevented due to interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from reagents.

It should be noted that SW-846 is subject to differing interpretations from the laboratories. In addition, the project-specific QAPP might include requirements which differ from those presented in this SOP. Therefore, some of the sections in this SOP may not be applicable to all situations.

II. HOLDING TIMES AND PRESERVATION

A. Review Items

Analytical result pages, Chain-of-Custody Records, raw data, and Case Narrative

B. Objective

The objective is to ascertain the validity of results based on the sample preservation techniques and the holding time of the sample from the time of collection to the time of analysis.

C. Criteria

Technical requirements for bottleware, chemical/temperature preservations, and sample holding times are based on the project-specific QAPP or the introductory material found in SW-846, Chapter Four, Organic Analytes, Section 4.1. The holding time criteria for chlorinated herbicides in cooled ($4° \pm 2°C$) water samples is seven days from sample collection to extraction and 40 days from sample extraction to analysis. The recommended holding times for solid samples is 14 days from sample collection to extraction and 40 days from sample extraction to analysis.

D. Evaluation

Technical holding times are established by comparing the sampling dates on the Chain-of-Custody forms with the dates of analysis on the analytical result pages and the raw data. Examine the sample records to determine if samples were preserved [cooled (4±2°C)]. Proper bottleware and sample preservation techniques are determined by reviewing the Chain-of-Custody Records and/or laboratory sample receipt logbook pages.

E. Action

If technical holding times are exceeded, document in the quality assurance review that holding times were exceeded and qualify the sample results according to the following criteria:

1. If extraction of aqueous samples was performed more than seven days and less than 14 days from the date of sample collection, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

2. If extraction of aqueous samples was performed more than 14 days from the date of collection, flag positive results as estimated (flagged "J") and "not-detects" as "R".

3. If the extracts for the aqueous samples were analyzed more than 40 days but less than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

4. If the extracts for the aqueous samples were analyzed more than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J" and "not-detects" as "R".

5. If extraction of solid samples was performed more than 14 days and less than 28 days from the date of sample collection, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

6. If extraction of solid samples was performed more than 28 days from the date of collection, flag positive results as estimated (flagged "J") and "not-detects" as "R".

7. If the extracts for the solid samples were analyzed more than 40 days but less than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

8. If the extracts for the solid samples were analyzed more than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "R".

9. If samples are received at temperatures greater than 10°C, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

10. If samples are collected in improper sample containers, professional judgment will determine the impact, if any, on the data. A noncorrectable deficiency may need to be written.

III. INITIAL CALIBRATION

A. Review Items

Analytical sequences, calibration summary forms, integration reports, and chromatograms

B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for organic compounds.

C. Criteria

1. Initial calibration standards containing the target compounds of interest are prepared according to the determinative method and are analyzed at five concentrations (whose range depends on the individual compound) at the beginning of each analytical sequence, or as necessary, if the continuing calibration acceptance criteria are not met. The low concentration standard should be at or near the method detection limit. The initial calibration standards will be used to define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with

check standards indicates a problem. It should be noted that the methods allow for either the internal or external standard method for quantitating positive results. Refer to the following table for criteria for the lowest point on the calibration curve:

Estimated Method Detection Limits for Method 8151, Diazomethane Derivatization

	Aqueous Samples	Soil Samples	
Analyte	GC/ECD Estimated Detection Limit[1] (µg/L)	GC/ECD Estimated Detection Limit (µg/Kg)	GC/MS Estimated Identification Limit (ng)
Acifluorfen	0.096		
Bentazon	0.2		
Chloramben	0.093	4.0	1.7
2,4-D	0.2	0.11	1.25
Dalapon	1.3	0.12	0.5
2,4-DB	0.8		
DCPA diacid	0.02		
Dicamba	0.081		
3,5-Dichlorobenzoic acid	0.061	0.38	0.65
Dichloroprop	0.26		
Dinoseb	0.19		
5-Hydroxydicamba	0.04		
MCPP	0.09	66	0.43
MCPA	0.056	43	0.3
4-Nitrophenol	0.13	0.34	0.44
Pentachlorophenol	0.076	0.16	1.3
Picloram	0.14		
2,4,5-T	0.08		
2,4,5-TP	0.075	0.28	4.5

[1] EDL = estimated detection limit; defined as either the MDL (40 CFR Part 136, Appendix B, Revision 1.11), or a concentration of analyte in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

a. The external standard calibration procedure is often used with GC work. This procedure works well with stable detectors, like an electron capture detector (ECD). An internal standard may be added by the laboratory to monitor the detector; however, with the external standard calibration procedure, internal standards are not used in sample result quantitation. Each compound in the external calibration standard is evaluated by a ration, known as a calibration factor (CF), of the area or height and the amount injected.

$$\text{Calibration Factor} = \frac{\text{Total Area or Height of Peak}}{\text{Mass Injected (in nanograms)}}$$

b. The internal standard calibration procedure is often used with GC/MS work. A known constant amount of one or more internal standards that are similar in analytical behavior to the compounds of interest is added to each calibration standard and diluted to volume with an appropriate solvent. The laboratory then calculates response factors (RFs) using the height or area responses against the concentration of each compound and internal standard.

$$RF = (A_s C_{is}) \; / \; (A_{is} C_s)$$

where:

A_s	=	Response for the analyte to be measured.
A_{is}	=	Response for the internal standard.
C_{is}	=	Concentration of the internal standards, µg/L.
C_s	=	Concentration of the analyte to be measured, µg/L.

2. The low standard must be visible on the chromatogram.

3. When the percent relative standard deviations (%RSDs) for the initial calibration standards are ≤20% for the compounds, linearity is assumed and the average calibration factor or response factor can be used in sample quantitations. If the RSD is in excess of 20%, then the calibration curve (binomial, cubic, quadratic, etc.) must be used for the particular compound.

However, the individual methods may indicate a calibration criteria which differs from this. Refer to the laboratory specific method in the QAPP for required calibration criteria.

D. Evaluation

1. Verify that the correct concentrations of standards were used for the initial calibration based on the laboratory analytical SOP and the determinative SW-846 method.

2. Verify that the correct initial calibration was used for all samples.

3. Verify if all sample results were calculated using the initial calibration in the proper way. Specifically, if the RSD for a particular compound is ≤20%, the average calibration factor or the average response factor should be used. If the RSD for a particular compound is >20%, the entire curve representing the working standards must be used.

4. Evaluate the initial calibration CFs or RFs for all target compounds.

   a. Check and recalculate the CFs and average CFs or the RFs and average RFs for three target compounds; verify that the recalculated value(s) agrees with the laboratory-reported value(s).

   b. Verify that the low calibration standard is clearly visible on the chromatogram.

5. Evaluate the %RSD for all target compounds.

   a. Check and recalculate the %RSD for three target compounds; verify that the recalculated values agree with the laboratory-reported values.

   b. If the average CF or average RF is used for quantitation, verify that all target compounds have a %RSD less than or equal to 20%.

   c. Visually verify that the calibration curve is an acceptable curve. Consult a senior quality assurance chemist if necessary.

E. Action

1. If any target compound result is associated with a low concentration initial calibration standard that is not visible on the chromatogram, professional judgment must be used to determine the magnitude of the bias. Flag "not-detects" for that compound with a "UJ". If the standards indicate a severe lack in sensitivity (e.g., the higher calibration standards are barely visible), the reviewer may elect to flag "not-detects" for that compound with an "R".

2. If any target compound has a %RSD greater than 20% and the average RF or CF was used for quantitation:

   a. Flag positive results for that compound as estimated (flagged "J").

   b. "Not-detects" for that compound may be qualified using professional judgment.

3. If the curve used for quantitation was deemed unacceptable:

   a. Flag the positive result for that compounds as estimated ("J").

   b. "Not-detects" for that compound may be qualified using professional judgment.

IV. CONTINUING CALIBRATION

A. Review Items

Analytical sequences, calibration summary forms, integration reports, and chromatograms

B. Objective

Continuing calibrations are performed to verify that the initial calibration curve is still acceptable for quantitation of results with respect to sensitivity and accuracy on a day-to-day basis. In addition, a quality control check sample (QCSS) is required containing each herbicide of interest (acid or ester) to establish the laboratory's ability to generate acceptable accuracy and precision.

C. Criteria

1. Continuing calibration standards containing target compounds and surrogate compounds are analyzed before and after all samples have been analyzed.

2. The concentration of the continuing calibration check must be at the midpoint of the curve.

3. For external calibrations, the working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±15%, a new calibration curve must be prepared for that analyte. (Note that several methods allow the analyst to reinject the standard to verify the noncompliant continuing calibration. Refer to the individual methods for specific calibration requirements.)

$$Percent\ Difference = \frac{R_1 - R_2}{R_1} \times 100$$

Where:

R_1 = Calibration Factor from first analysis.
R_2 = Calibration Factor from succeeding analyses.

4. For internal calibrations, the working calibration curve or response factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than ±15% (see formula above), a new calibration curve must be prepared for that compound.

5. The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory. All succeeding continuing calibrations after the first continuing calibration standard, used to establish daily

retention time windows, must be within the established retention time windows.

6. If any of the standards fall outside their daily retention time window, the system is out of control. The laboratory must determine the cause of the problem and correct it. All samples that were injected after the standard exceeding the criteria must be reinjected to avoid false negatives and possible false positives.

7. The QCCS should be prepared from a concentrate in acetone that is 1000 times more concentrated then the representative spike concentrations being measured. The data for the QCCS may or may not be included in the data package received for review. The acceptance criteria for precision and accuracy are found at the end of Method 8151 and in Section IV.D.5 below. If the acceptance criteria are not met for one or more target compounds, the system performance is unacceptable for that analyte. The QCCS analysis must then be repeated for the compound that failed to meet criteria. Repeated failure, however, would confirm a general problem with the measurement system. If this occurs, the laboratory should locate and correct the source of the problem, prepare a new QCCS, and repeat the test for all compounds of interest.

D. Evaluation

1. Verify that the continuing calibration was run at the required frequency and that the continuing calibration was compared to the correct initial calibration.

2. Evaluate the continuing calibration CF or RF for all target compounds.

   a. Quantitatively verify that the response factors were calculated properly; verify that the recalculated values agree with the laboratory-reported values. Recalculate three values for each continuing calibration.

   b. Verify that the peaks for the continuing calibrations are clearly visible on the chromatograms.

3. Evaluate the %D between the expected response from the initial calibration and the observed response from the continuing calibration for all compounds.

   a. Check and recalculate the %D on three target compounds; verify that the recalculated values agree with the laboratory-reported values.

   b. Verify that the %D is ≤15% for all target compounds.

4. Verify that after the daily retention time windows have been established (see Section X.C), all target analytes in the subsequent calibration checks are within the established retention time windows.

5. Evaluate the QCCS data, if provided, based on the following SW-846 acceptance criteria:

Accuracy and Precision for Method 8151 Diazomethane Derivatization, Organic-Free Reagent Water Matrix

Herbicide	Spike Concentration (µg/L)	Mean Percent Recovery	Standard Deviation of Percent Recovery
Acifluorfen	0.2	121	15.7
Bentazon	1	120	16.8
Chloramben	0.4	111	14.4
2,4-D	1	131	27.5
Dalapon	10	100	20.0
2,4-DB	4	87	13.1
DCPA diacid	0.2	74	9.7
dicamba	0.4	135	32.4
3,5-Dichlorobenzoic acid	0.6	102	16.3
Dichloroprop	2	107	20.3
Dinoseb	0.4	42	14.3
5-Hydroxydicamba	0.2	103	16.5
4-Nitrophenol	1	131	23.6
Pentachlorophenol	0.04	130	31.2
Picloram	0.6	91	15.5

Herbicide	Spike Concentration (µg/L)	Mean Percent Recovery	Standard Deviation of Percent Recovery
2,4,5-TP	0.4	117	16.4
2,4,5-T	0.2	134	30.8

Accuracy and Precision for Method 8151 Diazomethane Derivatization, Clay Matrix

Analyte	Mean Percent Recovery	Linear Concentration Range (ng/g)	Percent Relative Standard Deviation (n=20)
Dicamba	95.7	0.52-104	7.5
MCPP	98.3	620-61,800	3.4
MCPA	96.9	620-61,200	5.3
Dichloroprop	97.3	1.5-3,000	5.0
2,4-D	84.3	1.2-2,440	5.3
2,4,5-TP	94.5	0.42-828	5.7
2,4,5-T	83.1	0.42-828	7.3
2,4-DB	90.7	4.0-8,060	7.6
Dinoseb	93.7	0.82-1,620	8.7

Representative Recoveries of PFB Derivatives of Herbicides

Herbicide	Standard Concentration mg/L	% Recovery
MCPP	5.1	96.3
Dicamba	3.9	92.7
MCPA	10.1	90.2
Dichloroprop	6.0	88.3
2,4-D	9.8	70.0
Silvex	10.4	93.3
2,4,5-T	12.8	83.5
2,4-DB	20.1	95.0

E. Action

1. If initial or continuing calibrations were not performed at the specified frequency, a statement to this effect should be indicated in the quality assurance review. In addition:

   a. Flag positive results for that compound as estimated (flagged "J").

   b. Flag "not-detects" for that compound with a "UJ" or, in severe cases, "R".

2. If any target compound has a %D greater than 15% in either the continuing calibration before or after the applicable project samples:

   a. If positive results were reported from the GC column with the non-compliant standard, qualify positive results for that compound as estimated (flagged "J") on both sides of the noncompliant standard back to the last compliant calibration.

   b. "Not-detects" for that compound may be qualified "UJ" if the bias is in the direction of a sensitivity decrease. If the bias is in the direction of a sensitivity increase, data may be acceptable for "not-detected" sample results. In addition, "not-detects" for that compound may be qualified "UJ" if a tentative positive result is identified on the compliant column.

3. If any target compound is outside the daily established retention time windows, the associated sample chromatograms must be carefully evaluated using reviewer-generated expanded retention time windows.

   a. If the chromatograms reveal the absence of peaks possibly corresponding to the target compounds of interest using expanded retention time windows, data usability is not affected. A notation should be included in the quality assurance review.

   b. If the chromatograms reveal peaks corresponding to the target compounds of interest using expanded retention time windows, "not-detected", as well as reported positive sample results for the compound outside the retention time window, should be flagged

"R". This qualification is applicable to samples on both sides of the noncompliant standard back to the last compliant calibration.

4. If target analyte peaks in the continuing calibration are not visibly present on the chromatograms, "not-detected" sample results for those analytes should be flagged "R".

5. If the QCCS acceptance criteria are not met:
   a. Qualify positive results for those compounds as estimated (flagged "J") in all associated samples.

   b. "Not-detects" for that compound may be qualified "UJ" if the bias is in the direction of a sensitivity decrease. If the bias is in the direction of a sensitivity increase, data may be acceptable for "not-detected" sample results.

V. METHOD AND FIELD/EQUIPMENT BLANKS

A. Review Items

QC summary forms, chromatograms and integration reports

B. Objective

The assessment of blank analysis results determines the existence and magnitude of contamination problems. The analysis of a reagent blank can determine whether interferences from the analytical system, glassware, and reagents are under control. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting other data. If the laboratory blank (reagent blank) has reportable target analytes (at or above the RL), the entire sample batch is reextracted and reanalyzed.

C. Criteria

1. No contaminants should be found in the reagent blanks.

2. Each time a set of samples is extracted or there is a change in reagents, an organic-free reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

3. The reagent blank must be analyzed on each GC system used to analyze samples for each type of analysis.

D. Evaluation

1. Review the results of all associated blanks on the forms and raw data (chromatograms and integration reports) to evaluate the presence of target compounds in the blanks.

2. Verify that a reagent blank analysis has been reported for each extraction batch on each GC system used to analyze samples.

E. Action

If the appropriate blanks were not analyzed with the frequency described in Criteria 2 and 3 in Section V.C, then the reviewer should use professional judgment to determine if the associated sample data should be qualified.

Action in the case of unsuitable blank results depends on the origin and circumstances of the blank.

Positive sample results are not qualified for associated blank contamination unless the concentration of the compound in the sample is less than or equal to five times (5×) the amount for target compounds. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant. The results must not be corrected by subtracting any blank value.

Specific actions are as follows:

1. If a target compound is found in a blank but not found in the sample, no action is taken.

2. If the sample result is greater than the reporting limit (RL) but less than the required amount (5× the blank result), the sample results are qualified as "not-detected" ("U").

3. If the sample result is positive but less than the RL and is less than the required amount (5× the blank result), the result is raised to the RL and is flagged as "not-detected" ("U").

4. If the sample result is greater than the required amount (5× the blank result), the sample results are not qualified.

5. If gross blank contamination exists (e.g., saturated peaks on the GC), all affected compounds in the associated samples should be qualified as "R" due to interferences. Professional judgment must be exercised in these cases.

VI. SURROGATE RECOVERY

A. Review Items

QC summary forms, integration reports, and chromatograms

B. Objective

Laboratory performance (accuracy and extraction efficiency) on individual samples and blanks is established by means of spiking activities. All samples, standards, and blanks are spiked with one or two herbicide surrogate compound(s) prior to sample extraction. Deuterated target compounds should not be used as surrogates in GC analysis due to coelution problems. The recommended surrogate standard for use is 2,4-DCAA.

C. Criteria

1. One or more surrogate compound(s) is added to all samples, standards, and blanks prior to any extractions or esterifications/derivatizations to measure their recovery in environmental samples, standards, and blank matrices.

2. Recoveries for the surrogate compound are typically specified in the QAPP or by the laboratory. If recoveries are not specified in the method, some surrogate recovery criteria reported by the laboratory can be overly expanded. For data validation purposes, herbicide recovery criteria will be 50-150% for 2,4-DCAA and 28-141% for 2,4-DB.

D. Evaluation

1. Check raw data (e.g., chromatograms and integration reports) to verify the recoveries on the surrogate recovery QC summary form. When two GC columns were used in analysis, the lower of the two results may be reported on the QC summary form. Check for any calculation or transcription errors.

2. The following should be determined from the surrogate recovery QC summary form(s):

   a. If any surrogate compound recovery is below the acceptance criteria and only one GC column was used or only one GC column was used for sample quantitation, there should be a reanalysis to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies.

   b. When two GC columns are used for sample quantitations, the data reviewer should examine the raw data for all the surrogate recoveries. Often times, only the lower of the two surrogate recoveries is reported on the surrogate recovery QC summary form. If a surrogate compound recovery is below the acceptance criteria on both GC columns, there should be reanalysis to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies.

   c. The laboratory failed to perform appropriately if a surrogate recovery was below criteria with no evidence of reextraction and reanalysis. Be certain that the laboratory is utilizing a criterion for reextraction. Note: the laboratory's criterion may not necessarily be the guidance criterion stipulated in this SOP.

   d. Verify that no blanks have surrogate recoveries outside the criteria.

e. If the retention times of the surrogates are outside the retention time window, check the raw data for possible misidentification of GC peaks. Non-recovery of surrogates may be due to shift in retention time interference or dilutions.

f. Chromatograms are to be carefully scrutinized for possible interferences when surrogate recoveries are outside criteria. When interferences are observed that appear to have resulted in the laboratory reporting recoveries outside criteria, caution should be exercised in qualifying data. In the opinion of the chemist, if the recoveries were due to a matrix interference and not a bias within the surrogate compound retention time windows, data should not be qualified. Furthermore, the decision must be fully documented (e.g., include chromatogram with comments) in the Support Documentation. In the event that the interference has affected the successful field analysis for target compounds, refer to the "Target Compound Identification" section of this SOP.

g. No qualification of data is necessary if the surrogate is diluted beyond detection. When multiple confounding issues are present, discussion should be presented in the Support Documentation, providing rationale (> 5-fold dilution) for any qualifications or lack of qualifications.

E. Action

Data are qualified based on surrogate compound results if the recovery for the surrogate compound is out of specification and interferences are not evident. For surrogate compound recoveries out of specification, the following approaches are suggested:

1. When one GC column is used and the surrogate recovery is greater than the upper acceptance limit:

   a. Positive target compounds are qualified as estimated (flagged "J").

   b. "Not-detected" results for target compounds should not be qualified.

2. When two GC columns are used and a surrogate recovery is greater than the upper acceptance limit on both GC columns or only on the GC column used for sample quantitations:

   a. Positive target compounds are qualified as estimated (flagged "J").

   b. "Not-detected" results for target compounds should not be qualified.

3. When one GC column is used and the surrogate recovery is greater than or equal to 10% for herbicides but less than the lower acceptance limit:

   a. Positive target compounds are qualified as estimated (flagged "J").

   b. "Not-detected" results for target compounds should be qualified "UJ".

   Note: when there is an unacceptable surrogate compound recovery followed by successful reextraction/reanalysis, the laboratory is often required to report only the results for the successful run.

4. When two GC columns are used and a surrogate recovery is greater than or equal to 10% for herbicides, but less than the lower acceptance limit on both GC columns, or only on the GC column used for sample quantitations:

   a. Positive target compounds are qualified as estimated (flagged "J").

   b. "Not-detected" results for target compounds should be qualified "UJ".

5. When one GC column is used and the surrogate has a recovery less than 10% for herbicides:

   a. Positive target compound results are qualified as estimated (flagged "J").

   b. "Not-detected" results for target compounds should be qualified "R".

6. When two GC columns are used and a surrogate recovery is less than 10% for herbicides on both GC columns, or only on the GC column used for sample quantitations:

   a. Positive target compound results are qualified as estimated (flagged "J").

   b. "Not-detected" results for target compounds should be qualified "R".

7. Often, sample chromatograms must be examined and professional judgment utilized to best qualify data based on surrogate recoveries. The following tables represent further examples of situations that may arise when two surrogates are spiked onto separate GC columns. The recoveries listed for SURR1 and SURR2, respectively, are representative of a recovery <u>on a column</u> (A or B). Therefore, the recoveries of SURR1 can be interchanged with SURR2 recoveries <u>on a column</u> with the same qualification resulting. The three tables are designed to emphasize very low recoveries (<10%), low recoveries (10% <%R <50%) and high recoveries (>135%).

Assuming No Interference				
SURR 1A	SURR 1B	SURR 2A	SURR 2B	<10%
<10% <10%	<10% ?	? ?	? <10%	Positive results: "J" "Not-detects": "R"
<10%	<50%*	?	>10%	Positive results: "J" "Not-detects:" No tentative (+) on either column - "UJ" Tentative (+) on column A, not confirmed on column B - "UJ"; Tentative (+) on column B, not confirmed on column A - "R"
<10%	Acceptable	?	Acceptable	Positive results: Reported from column A - "J" Reported from column B - no qualification "Not-detects": No qualification <u>except</u> tentative (+) on column B, not confirmed on column A - "R"
<10%	>135%	?	>10%	Positive results: J "Not-detects": No qualification <u>except</u> tentative (+) on column B, not confirmed on column A - "R"

* Assumes >10%

? It does not matter what this recovery is.

Assuming No Interference				
SURR 1A	SURR 1B	SURR 2A	SURR 2B	<50%*
<50%* <50%*	<50%* >10%	>10% >10%	>10% <50%**	Positive results: "J" "Not-detects": "UJ"
<50%*	Acceptable	>10%	Acceptable	Positive results: Reported from column A - "J"; Reported from column B - no qualification. "Not-detects": No qualification except tentative (+) on column B; Not confirmed on column A - "UJ"
<50%*	>135%	>10%	>50%	Positive results: J "Not-detects": No qualification except tentative (+) on column B; Not confirmed on column A - "UJ"

* Assumes >10%

Assuming No Interference				
SURR 1A	SURR 1B	SURR 2A	SURR 2B	>135%
>135% >135%	>135% >50%	>50% >50%	>50% >135%%	Positive results: "J" "Not-detects": No qualification
>135%	Acceptable	>50%	Acceptable	Positive results: Reported from column A - "J"; Reported from column B - No qualification.

VII. MATRIX SPIKES/MATRIX SPIKE DUPLICATES

A. Review Items

QC summary forms, chromatograms, and integration reports

B. Objective

Data for matrix spikes (MSs)/matrix spike duplicates (MSDs) are generated to determine long-term accuracy and precision of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the

time of sample analysis. These data alone are not used to evaluate the accuracy of other samples. For soil and waste samples where detectable amounts of herbicides are present, replicate samples may be appropriate in place of spiked duplicates.

C. Criteria

1. MS/MSD samples are analyzed at a frequency of one per 20 samples.

2. MS/MSD recoveries and MS/MSD RPDs should be within the QC acceptance criteria described below:

Representative Recoveries of PFB Derivatives of Herbicides

Herbicide	% Recovery Range	Maximum %RPD
2,4-D	41-127%	32%
silvex	46-137%	39%
2,4,5-T	36-126%	29%
dinoseb	74-98%	50%

D. Evaluation

1. Verify that the MS/MSD pair was analyzed at the required frequency.

2. Inspect results for the MS/MSD recoveries and the MS/MSD RPDs on the QC summary forms and verify that the results for the recoveries are within the specified limits.

3. Verify transcriptions from raw data and verify calculations.

4. Calculate the RSD for the positive results of unspiked compounds in the initial and MS/MSD analyses.

E. Action

1. No action is taken on MS/MSD data alone. However, using informed professional judgment, the data reviewer may use the MS/MSD results in

conjunction with the other QC criteria and determine the need for some qualification of the data.

2. In the instance where it can be determined that the results of the MS/MSD affect only the sample spiked, the following criteria should be used for the sample that was spiked.

   a. If the recovery of a matrix spike compound in the MS/MSD has a recovery greater than the upper acceptance limit, positive results for that compound in the unspiked sample should be considered estimated (flagged "J").

   b. If the recovery of a matrix spike compound in the MS/MSD has a recovery less than the lower acceptance limit and >10%, the positive result for that compound in the unspiked sample should be considered estimated (flagged "J") or the "not-detected" result should be flagged "UJ".

   c. If the recovery of a matrix spike compound in the MS/MSD has a recovery less than 10%, positive results for that compound in the unspiked sample should be considered estimated (flagged "J") and "not-detected" results should be flagged "R".

   d. If the RPD is outside the acceptance criteria, positive sample results for those analytes should be considered estimated and flagged "J".

3. If the RSD for the positive results for an unspiked target compound in the initial and MS/MSD analyses exceeds 30%, flag the positive result for the compound in the initial sample analysis as estimated ("J"). Exception: if one or more of the results in the initial and MS/MSD analyses is less than 5×RL, flag the positive result in the initial sample analysis "J" if the three results fall outside a 2×RL window.

VIII. BLANK SPIKES/LABORATORY CONTROL SAMPLES

A. Review Items

QC summary forms, chromatograms, and integration reports

B. Objective

The data for blank spikes (BSs), laboratory control samples (LCSs), or QC reference standards are generated to determine analytical accuracy. The results of blank spikes are used to assess the accuracy of the entire sample batch.

C. Criteria

1. The QC reference standard (or BS or LCS) must be analyzed for each target compound that fails the MS/MSD acceptance criteria. Due to the number of compounds being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory, the probability that the analysis of a QC reference standard (or BS or LCS) will be required is high. Therefore, the QC reference standard (or BS or LCS) is often routinely analyzed with the spiked sample.

2. The QC reference standard (or BS or LCS) recoveries should be within the QC acceptance criteria for matrix spike/matrix spike duplicate analyses described in the previous section. If the recovery of any such compound falls outside the designated range, the laboratory performance for that compound is judged to be out of control, and the problem should be immediately identified and corrected. The result for that compound in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

3. If any recovery is below the acceptance criteria (laboratory-generated only) in the QC reference standard (or BS or LCS) analysis, all associated samples must be reextracted and reanalyzed.

D. Evaluation

1. Verify that a QC reference standard (or BS or LCS) was analyzed at the required frequency.
2. Inspect results for the QC reference standard (or BS or LCS) recoveries on the QC summary forms and verify that the results for the recoveries are within the specified limits.

3. Verify transcriptions from raw data and verify calculations.

E. Action

1. Action may be taken on the entire batch based on the QC reference standard (or BS or LCS) recoveries.

2. In instances where the QC reference standard (or BS or LCS) recoveries are outside acceptance criteria, the following criteria are applied to all samples (of similar matrix) in that extraction batch:

   a. If the recovery of a spike compound in the QC reference standard (or BS or LCS) has a recovery greater than the upper acceptance limit, positive results for that compound in the unspiked sample should be considered estimated (flagged "J").

   b. If the recovery of a spike compound in the QC reference standard (or BS or LCS) has a recovery less than the lower acceptance limit and $>10\%$, the positive result for that compound in the unspiked sample should be considered estimated (flagged "J") or the "not-detected" result should be flagged "UJ".

   c. If the recovery of a spike compound in the QC reference standard (or BS or LCS) has a recovery less than 10%, positive results for that compound in the unspiked sample should be considered estimated (flagged "J") and "not-detected" results should be flagged "R".

   d. In some instances, the laboratory may run duplicate QC reference standard (or BS or LCS) analyses. Compare these results using the same criteria as with MS/MSDs. If the RPD is outside the acceptance criteria, positive sample results for those analytes in <u>all</u> associated samples should be considered estimated and flagged "J".

IX. INTERNAL STANDARDS (if used)

A. Review Items

QC summary forms, integration reports, and chromatograms

B. Objective

Internal standards performance criteria ensures that GC sensitivity and response are stable during each analysis. Internal standards are used for the quantitation of positive results of all compounds and surrogates in the analysis. The internal standard must not be affected by method or matrix interferences. The compound 4,4'-dibromooctafluorobiphenyl (DBOB) has been shown to be an effective internal standard, but other compounds, such as 1,4-dichlorobenzene, may be used if there is a DBOB interference. Usually, internal standards are used for GC/MS analyses and not for GC analyses.

C. Criteria

1. Internal standard compounds are added to all field samples, QC samples, and blanks immediately before injection into the GC to ensure that sensitivity and response are stable during each analysis.

2. Criteria for internal standards are typically specified in the QAPP or by the laboratory. If criteria are not specified, utilize the following guidance:

   Retention times of the internal standards in the samples and blanks must not vary more than ±30 seconds from the retention times of the associated calibration standard, and the area counts of the internal standards in the samples and blanks must not vary more than a factor of two (-50% to +100%) from the associated calibration standard for all samples.

D. Evaluation

1. Verify that internal standard compounds were added to all samples and blanks if the internal standard method of quantitation is used for the analysis.

2. If any internal standard compound is outside the acceptance criteria (laboratory-specified), there should be a reanalysis to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies.

E. Action

Data are qualified if internal standard compound results are out of specification. For internal standard compounds out of specification, the following approaches are suggested:

1. If an internal standard area count for a sample is greater than the upper acceptance limit, flag positive results "J" and "not-detected" results "UJ" for the compounds quantitated from the internal standard.

2. If an internal standard area count for a sample is less than the lower acceptance limit but greater than or equal to 10% of the associated calibration internal standard, flag positive results "J" and "not-detected" results "UJ" for the compounds quantitated from the internal standard.

3. If an internal standard area count for a sample is less than 10% of the associated calibration internal standard, flag positive results "J" and "not-detected" results "R" for the compounds quantitated from the internal standard.

4. When the internal standard retention time varies by more than 30 seconds and no peaks are observed in the sample chromatogram, then there may be no impact on data usability. However, if peaks are observed in the sample chromatogram, professional judgment will be exercised on a case-by-case basis.

X. TARGET COMPOUND IDENTIFICATION

A. Review Items

QC summary forms, Case Narratives, integration reports, and chromatograms

B. Objective

The objective is to ensure that the compound identifications are accurate based on retention time windows, peak resolution, and the linear range of the system.

C. Criteria

1. Retention time windows must be established to ensure the GC system is within optimum operating conditions. Ideally, the laboratory makes three injections of all herbicide standard mixtures throughout the course of a 72-hour period. Serial injections over less than a 72-hour period result in retention time windows that are too tight. The laboratory then calculates the standard deviation of the three retention times (use any function of retention time, including absolute retention time or relative retention time) for each herbicide standard.

2. Daily retention time windows should be established for each herbicide compound. The retention time for each herbicide mentioned above is used as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined above. Refer to the tables in Method 8151 which list retention times for the herbicides after esterification, using the diazomethane derivatization procedure and the PFB derivatization procedure, respectively.

3. Tentative identification of a herbicide occurs when a peak from a sample extract falls within the daily retention time window. Normally, confirmation is required on a second GC column. Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses.

4. If the target compound peak responses exceed the linear range of the calibration curve, the extracts should be diluted and reanalyzed. All peaks should be on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration. If peak detection is prevented by the presence of interferences, further cleanup is required.

5. GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Refer to Method 8270 for the appropriate GC/MS operating conditions and analysis procedures. When available, chemical ionization mass spectra may be employed to aid the qualitative identification process. If these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These

steps may include the use of alternate packed or capillary GC columns, or additional cleanup.

D. Evaluation

1. Second-column confirmation should be provided; if it was not, attempt to obtain the confirmation analysis from the laboratory. If the confirmation analysis cannot be provided or was not performed, write a comment in the quality assurance review.

2. Verify that the target compound peaks have unique retention time (RT) windows by viewing the initial calibration standards or any RT window summary information that the laboratory may have provided.

3. Verify that for any target compound responses exceeding the linear range of the calibration curve, the extracts were diluted and reanalyzed for those particular compounds.

4. Study the chromatograms for unstable baselines, coeluting peaks, poor resolution, matrix interferences, or any other problems that would hinder the identification of target compounds (producing false negatives or false positives).

5. If GC/MS techniques were employed, the mass spectra must be examined to confirm the laboratory's peak identifications. The spectra should show similar molecular ion peaks (after background subtraction) eluting in the herbicide peak in the reference standard and the herbicide peak in the sample. The intensity of molecular ion peaks should be proportionally the same between the reference standard and the sample to demonstrate identical fragmentation patterns for the herbicide compound.

E. Action

Data qualification is based on professional judgment upon evaluation of the sample data. The following approaches are suggested:

1. If the sample results were not confirmed on a second column, flag positive results "J" and "not-detected" results "UJ".

2. If any reported target compound peak is not within the RT window, evaluate the surrogate peaks for similar RT shifting. If none is observed, flag reported results "R".

3. If a target compound response exceeded the linear range of the calibration curve and the extract was not diluted and reanalyzed, flag the reported positive results "J".

4. If there is a poor GC/MS identification of an analyte (if GC/MS is performed), flag the positive results as "J". If the reported target compound peak is also not within the RT window, flag reported positive results "R".

XI. COMPOUND QUANTITATION AND REPORTED REPORTING LIMITS

A. Review Items

QC summary forms, Case Narrative, integration reports, and chromatograms

B. Objective

The objective is to ensure that reported quantitative results and reported reporting limits (RLs) are accurate.

C. Criteria

1. Compound quantitation, as well as the adjustment of the RLs, must be calculated according to the correct equation specified in the analytical SOP.

2. The compound quantitation must be based on the average CF or RF from the four initial calibration standards if the RSD is $<20\%$. If the RSD is $>20\%$, the initial calibration curve must be used for quantitation.

3. If calibration standards have been analyzed in the same manner as the samples (e.g., have undergone hydrolysis and esterification), compound quantitation based on the average CF or RF must be calculated according to the following equations:

External Standard Calibration Equations:

Aqueous Samples:

$$\text{Concentration } (\mu g/L) = [(A_x)(V_t)(D)]/[(CF)(V_i)(V_s)]$$

Where:

A_x = Response for the analyte in the sample, units may be in area counts or peak height.

CF = Average Calibration factor.

V_i = Volume of extract injected, µL. For purge-and-trap analysis, V_i is not applicable and therefore = 1.

D = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, D = 1.

V_t = Volume of total extract, µL. For purge-and-trap analysis, V_t is not applicable and therefore = 1.

V_s = Volume of sample extracted or purged, mL.

Solid Samples:

$$\text{Concentration } (\mu g/Kg) = [(A_x)(V_t)(D)]/[(CF)(V_i)(W)]$$

where:

W = Weight of sample extracted or purged, g. The wet weight or dry weight may be used, depending upon the specific applications of the data.

A_x, CF, V_t, D, and V_i have the same definition as for aqueous samples when a solid sample is purged (e.g., low concentration soil) for volatile organic analysis or for semivolatile organic and pesticide extracts. When the nonaqueous sample is extracted for purge and trap analysis, V_i = volume of methanol extract added to reagent water for purge and trap analysis.

Internal Standard Calibration Equations:

Aqueous samples:

Concentration ($\mu g/L$) = $[(A_x)(C_{is})(D)]/[A_{is})(RF)(V_s)]$

where:

A_x = Response of the analyte being measured, units may be in area counts or peak height.

C_{is} = Amount of internal standard added to extract or volume purge, ng.

D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1.

A_{is} = Response of the internal standards, units same as A_x.

RF = Average response factor for compound.

V_s = Volume of water extracted or purged, mL.

Solid Samples:

Concentration ($\mu g/Kg$) = $[(A_s)(C_{is})(D)]/[(A_{is})(RF)(W_s)]$

W_s = Weight of sample extracted, g. Either a dry weight or wet weight may be used, depending upon the specific application of the data.

A_s, C_{is}, D, A_{is}, and RF have the same definition as for aqueous samples.

4. If calibration is performed using standards made from methyl ester compounds (compounds not esterified by application of this method), then the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide. Typically, a correction factor, as described below, is added to the numerator in the aforementioned concentration equation above.

$$\text{Correction Factor} = R/[R + 14]$$

Where:

R = Molecular weight of acid herbicide.

5. Verify that the correct RFs are used for quantitation. Verify that the same RFs are used consistently throughout, in both the calibration as well as the quantitation process.

6. Verify that the RLs have been adjusted to reflect all sample dilutions that are not accounted for by the method.

E. Action

If reporting limits reported by the laboratory exceed the QAPP-specified reporting limits, and if no sample dilutions were necessary, or if no matrix-related interferences were observed, professional judgment should be used to assess the validity of the elevated sample results. The problem must be noted in the quality assurance review.

If any discrepancies are found, the laboratory may be contacted by the designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unsolved, the reviewer must use professional judgment to decide which value is the best value. Under these circumstances, the reviewer may determine if qualification of data is warranted.

XII. LABORATORY DUPLICATES

A. Review Items

Analytical result forms, chromatograms, and integration reports

B. Objective

Laboratory duplicate samples may be taken and analyzed as an indication of overall laboratory prevision and performance. As mentioned before, for soil and waste samples where detectable amounts of herbicides are present, replicate samples (laboratory duplicates) may be appropriate in place of spiked duplicates.

C. Criteria

There are no specific review criteria for laboratory duplicate analyses comparability within the published methods. However, the QAPP should define the laboratory duplicate criteria for solid and aqueous samples as part of the data quality objectives.

D. Evaluation

The reviewer should compare the results reported for each sample and duplicate on the QC summary form and calculate the relative percent difference (RPD).

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met:

1. A control limit of ±20% (±40% for solids) for the RPD shall be used for sample values greater than 5× the RL.

2. A control limit of ± 2× the RL shall be used for sample values less than 5× the RL.

XIII. FIELD DUPLICATES

A. Review Items

Analytical result forms, chromatograms, and integration reports

B. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates, which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

C. Criteria

There are no specific review criteria for field duplicate analyses comparability within the published methods. However, the QAPP should define the field duplicate criteria for solid and aqueous samples as part of the data quality objectives.

D. Evaluation

Samples which are field duplicates must be identified by reviewing the Chain-of-Custody Records or by contacting the client. The reviewer should compare the results reported for each sample and duplicate and calculate the relative percent difference (RPD).

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met:

1. A control limit of $\pm 20\%$ ($\pm 40\%$ for solids) for the RPD shall be used for sample values greater than $5\times$ the RL.

2. A control limit of $\pm$ $2\times$ the RL shall be used for sample values less than $5\times$ the RL.

XIV. SYSTEM PERFORMANCE

A. Review Items

QC summary forms and raw data

B. Objective

During the period following instrument performance QC checks (e.g., blanks and calibration standards), changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

C. Criteria

There are no specific criteria for system performance. Professional judgment should be applied to assess the system performance.

D. Evaluation

1. Abrupt, discrete shifts in the chromatogram baseline may indicate a change in the instrument's sensitivity or the baseline setting. A baseline "shift" could indicate a decrease in sensitivity in the instrument or an increase in the instrument baseline, possibly causing target compounds, at or near the detection limit, to miss detection. A baseline "rise" could indicate problems such as a change in the instrument baseline, a leak or degradation of the column.

2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   a. High background levels or shifts in absolute retention times for calibration standards.

   b. Excessive baseline rise.

   c. Extraneous peaks.

d. Loss of resolution.

e. Peak tailing or peak splitting that may result in inaccurate quantitation.

E. Action

Professional judgment must be used to qualify the data if it is determined that system performance has degraded during sample analyses. The data reviewer must use all the information available (surrogate recoveries, MS/MSD analyses, LCSs, etc.) to try to ascertain the effect of baseline or resolution problems which may have occurred during the analysis.

XV. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results, QAPP, and Sampling and Analysis Plan

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the client in avoiding inappropriate use of the data.

Review all available information, including the QAPP, Sampling and Analysis Plan, and communications with the client that concerns the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Prepare a fully documented quality assurance review which provides the client with an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his assessment of the usability of the data within the given context.

XVI. AUTHORITY

This data validation SOP for the analysis for chlorinated herbicides by GC/ECD (SW-846 Method 8151) has been prepared by Environmental Standards, Inc. for the 3M Corporation Cordova project. This SOP is not to be used for any other project or used by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date:_____

Rock J. Vitale, CPC
Director of Chemistry

STANDARD OPERATING PROCEDURES FOR DATA VALIDATION OF INORGANICS (METALS AND CYANIDE) BY SW-846 METHODS*

I. METHOD SUMMARY

A. ICP Analysis and Atomic Emission Spectrometric Analysis

Aqueous samples: 100 mL sample is heated with acid, filtered, and adjusted back to 100 mL.

Solid samples: 1.0 grams of sample is heated with acid, filtered, and adjusted to 200 mL volume.

Samples, once solubilized or digested, are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific, atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes.

B. Mercury Analysis by Cold Vapor Technique

Aqueous samples: 100 mL of sample are digested with acid.

Solid samples: 0.2 grams of solid sample are digested with acid.

Mercury is reduced to the elemental state in the samples and is aerated from solution. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded.

C. Cyanide Analysis

250 mL of aqueous sample or 5 grams of solid sample added to 250 mL of water are treated with acid. Cyanide, as hydrocyanic acid, is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or calorimetrically.

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* **See Section XIV for Authority and Application of this SOP.**

II. TECHNICAL HOLDING TIMES

A. Review Items

Analytical Results Summaries (Form I's), Chain-of-Custody forms, digestion or distillation logs, and Case Narrative

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to time of analysis.

C. Criteria

Technical requirements for sample holding times have only been established for water matrices. The technical holding time criteria for water samples from date of sample collection are as follows:

Metals: 6 months; preserved to pH <2 with HNO_3

Mercury: 28 days; preserved to pH <2 with HNO_3

Cyanide: 14 days; preserved to pH >12 with NaOH, cool to $4 \pm 2°C$

D. Evaluation Procedure

Technical holding times are established by comparing the sampling dates on the Chain-of-Custody forms with the dates of analysis on the Form I's and the raw data. Examine the sample records to determine if samples were preserved.

E. Action

If technical holding times are exceeded, document in the quality assurance review that holding times were exceeded and qualify the sample results according to the following criteria:

1. If holding times and preservation criteria (chemical and temperature) are not met, all positive results should be qualified "J", estimated, and all "not-detected" results should be qualified "UJ".

2. If holding times are grossly exceeded (analyzed outside 2× the holding time criteria), the reviewer may use professional judgment and qualify results < IDL as unusable ("R") and positive results as estimated ("J").

3. If the temperature of the samples for cyanide analysis was reported to be greater than 6°C upon receipt at the laboratory, ascertain how the sample temperature was taken. If the laboratory used a temperature bottle or an IR gun to determine sample temperature, include a note of this deficiency in the QA report. If the temperature of the samples for cyanide analysis exceeds 10°C, qualify the positive results as estimated ("J") and "not-detected" results as "UJ".

III. CALIBRATION

A. Review Items

Calibration forms (Form IIs) and raw calibration data

B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analysis run, and continuing calibration verification documents that the initial calibration is still valid.

C. Criteria

1. Initial Calibration

Instruments must be calibrated daily and each time the instrument is set up.

a. ICP Analysis

A blank and at least three standards must be used in establishing the analytical curve. The high concentration standard must then be reanalyzed, and recoveries within 5% of the true value must be obtained.

b. Atomic Absorption Analysis (AA)

1) A blank and at least three standards, one of which must be at the reporting limit, must be used in establishing the analytical curve.

2) The correlation coefficient must be ≥ 0.995.

c. Mercury Analysis

1) A blank and at least four standards must be used in establishing the analytical curve. One standard should be at the reporting limit.

2) The correlation coefficient must be ≥ 0.995.

d. Cyanide Analysis

1) A blank and at least three standards must be used in establishing the analytical curve. One standard must be at the reporting limit.

2) A midrange standard must be distilled.

3) The correlation coefficient must be ≥ 0.995.

2. Initial and Continuing Calibration Verification (ICV and CCV)

a. Analysis results must fall within the control limits of 90-110% recovery (%R) of the true value for all analytes except mercury and cyanide.

b. Analysis results for mercury must fall within the control limits of 80-120% R.

c. Analysis results for cyanide must fall within the control limits of 85-115% R.

d. An EPA-certified standard must be used for the Initial Calibration Verification (ICV) and must be analyzed immediately following instrument calibration for each wavelength used for analysis.

e. A CCV must be analyzed every ten samples. The CCV must also be analyzed at the beginning and the end of the analytical sequence.

f. To verify linearity near the reporting limit for ICP analysis, the contractor may analyze a standard at 2 times the reporting limit or 2 times the IDL, whichever is greater.

D. Evaluation Procedure

1. Verify that the instrument was calibrated daily and each time the instrument was set up using the correct number of standards and a blank.

2. Verify that the correlation coefficient is ≥ 0.995 for all AA, Hg, and CN analyses.

3. Check the distillation log and verify that the midrange CN standard was distilled.

4. Verify that a standard at the reporting limit was used in the AA and cyanide calibration curve or that a standard at the reporting limit was analyzed at the beginning of the analysis run.

5. Verify that an EPA-certified standard was used for the ICV for all analyses.

6. Verify that all ICV and CCV recoveries fall within the required windows.

7. Check the raw data to verify that the calibration standard values were transcribed correctly on to Form IIs. Recalculate one or more of the ICV and CCV percent recoveries (%R) and verify that the recalculated value agrees with the laboratory reported values on the Form IIs.

8. Verify that a CCV was analyzed every 10 samples.

9. Verify that a standard at 2× reporting limit was analyzed to verify linearity near the IDL for ICP analysis.

E. Action

1. If the appropriate number of standards were not used for initial calibration or if the instrument was not calibrated daily and each time the instrument was set up, qualify the data as unusable ("R").

2. If a standard at the reporting limit was not used in establishing the calibration curve for AA, positive results up to 2× reporting limit and "not-detects" results may have to be flagged as estimated. Examine the recoveries of any low-level standards analyzed during the analysis scheme in order to make judgments on the accuracy of the calibration curve at the low end.

3. If the correlation coefficient is <0.995 for AA, Hg, or CN, qualify positive results as estimated ("J") and "not-detects" as "UJ".

4. If a midrange standard for cyanide was not distilled before analysis or did not meet the 10% criteria, qualify all associated positive results as estimated ("J").

5. If the ICV or CCV %R falls outside the acceptance windows, use professional judgment to qualify all associated data. The following guidelines are recommended:

   a. If the ICV or CCV %R falls outside the acceptance windows but within the ranges of 75-89% or 111-125% (CN, 70-84% or 116-130%; Hg, 65-79% or 121-135%), qualify positive results as estimated ("J").

   b. If the ICV or CCV %R is within the range of 111-125% (CN, 116-130%; Hg, 121-135%), "not-detected" results are acceptable.

   c. If the ICV or CCV %R is 75-89% (CN, 70-84%, Hg, 65-79%), qualify "not-detected" results as estimated ("UJ").

   d. If the ICV or CCV %R is $<75\%$ (CN, $<70\%$; Hg, $<65\%$), qualify all positive results and "not-detected" results as unusable ("R").

e. If the ICV or CCV %R is >125%, (CN, >130%; Hg >135%), qualify positive results as unusable ("R"); "not-detected" results are acceptable.

IV. BLANKS

A. Review Items

Blank Summaries (Form IIIs), Form I's and raw data.

B. Objective

The assessment of blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. Criteria

1. No contaminants should be found in the blank.

2. A preparation blank must be analyzed for each matrix, for every 20 samples digested, or for each batch digested, whichever is more frequent.

3. A calibration blank (CCB) must be analyzed after every ten samples. The CCB must also be analyzed before the analytical sequence and at the end of the analytical sequence.

D. Evaluation Procedure

1. Review the results reported on the Form III as well as the raw data for all blanks and verify that the results were accurately reported.

2. Verify that the calibration blanks and preparation blanks were analyzed at the proper frequency.

E. Action

1. Action in the case of unsuitable blank results depends on the circumstances and origin of the blank. Any blank with a value below the negative reporting limit must be carefully evaluated to determine its effect on the sample data.

2. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The result must not be corrected by subtracting any blank value. Action levels should be calculated that are 5 times the maximum concentration of each contaminant detected in any blank. No positive results should be reported unless the concentration of the analyte in the sample exceeds 5 times the amount detected in any blank.

NOTE: The reviewer should note that the blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. In particular, solid sample results reported on the Form I's will not be on the same bases (units, dilutions) as the calibration blank data reported on the Form IIIs. Sample weights, volumes, and dilution factors must be taken into consideration when applying the 5× criteria.

Sample results should be reported as follows:

a. If an analyte is detected in the blank but not in the sample, no action is taken.

b. Positive results less than the action level shall be reported with a "U".

c. Positive results greater than the action level shall be reported unqualified.

V. ICP INTERFERENCE CHECK SAMPLE ANALYSIS

A. Review Items

ICP Interference Check Summaries (Form IVs) and raw data

B. Objective

The ICP Interference Check Sample (ISC) analysis is performed to verify the contract laboratory's interelement and background correction factors.

C. Criteria

1. An ICS analysis must be run at the beginning and end of each sample analysis run or a minimum of twice per 8 hour working shift, whichever is more frequent.

2. Results for the ICS solution AB analysis must fall within the control limits of ± 20% of the true value.

3. Results for the non-interfering elements with reporting limits less than 10 µg/L must fall within ±2× the reporting limit in the ICSA and ICSAB.

D. Evaluation Procedure

1. Verify that the ICS was analyzed at the proper frequency.

2. Verify that the %R for the ICSA and ICSAB is 80-120%

3. Recalculate from the raw data one or more recoveries and verify that their calculated value agrees with the laboratory reported values on the Form IV.

4. Check ICSA and AB raw data for results with an absolute value above the reporting limit for those analytes which are not present in the ICSA and ICSAB solution. Results greater than twice the absolute value of the reporting limit indicate either a positive or negative interference and must be qualified.

E. Action

1. If the ICS was not analyzed at the proper frequency, the data may be affected. Use professional judgment to qualify the data.

2. For samples with concentrations of Al, Ca, Fe, and Mg which are comparable to or greater than their respective levels in the ICS:

a. If the ICSAB recovery for an element is >120% and the reported sample results are below the reporting limit, this data is acceptable for use.

b. If the ICSAB recovery for an element is >120% and the reported sample results are above the reporting limit, qualify the affected data as estimated ("J").

c. If the ICSAB recovery for an element falls between 50% and 79% and reportable quantities of the analyte were detected, qualify the affected data results as estimated ("J").

d. If an analyte is not detected in the sample and the ICSAB recovery for that analyte falls within the range of 50-79%, the possibility of false negatives may exist. Qualify the data for these samples as estimated ("UJ").

e. If the ICSAB recovery results for an element are <50%, qualify the affected data as unusable ("R").

3. If results above the reporting limit are observed for elements which are not present in the EPA-provided ICS solution, the possibility of false positives exists. An evaluation of the associated sample data for the affected elements should be made. For samples with comparable or higher levels of interferences, sample results above the reporting limit which approximate (within 10 times) those levels found in the ICS (false positives) should be qualified as estimated ("J").

4. If results less than the negative are observed for elements which are not present in the EPA ICS solutions, the possibility of false negatives in the samples may exist. If the absolute value of the negative results is above the reporting limit, an evaluation of the associated sample data should be made. For samples with comparable or higher levels of interferents, all results for the affected analytes which are reported as less than the reporting limit should be qualified as estimated ("UJ"), and positive results reported at levels less than 10× the observed ICSA or ICSAB concentration (absolute value) should be quantitated as estimated.

5. In general, the sample data can be accepted if the concentration of Al, Ca, Fe, and Mg in the sample are found to be less than or equal to their

respective concentrations in the ICS. If other elements are present in the sample at > 10 mg/L, the reviewer should investigate the possibility of other interference effects. These analyte concentration equivalents presented in SW-846 Method 6010A should be considered only as estimated values, since the exact value of any analytical system is instrument-specific. Therefore, estimate the concentration produced by an interfering element. If the estimate is >2× reporting limit and also greater than 10% of the reported concentration of the affected element, qualify the affected results as estimated ("J").

VI. LABORATORY CONTROL SAMPLE ANALYSIS (LCS)

A. Review Items

Laboratory Control Sample Summaries (Form VII) and raw data

B. Objective

The laboratory control sample analysis is designed to serve as a monitor of the efficiency of the digestion procedure.

C. Criteria

1. All aqueous LCS results must fall within the control limits of 80-120%R. Antimony and silver are excluded from this criteria contractually. An aqueous LCS analysis is not required for mercury or cyanide.

2. All solid LCS results must fall within the control limits established by the EPA.

D. Evaluation Procedure

1. Review Form VIIs and verify that results fall within the control limits.

2. Check the raw data to verify reported results on Form VIIs. Recalculate one or more of the recoveries.

3. Verify that an LCS was prepared and analyzed at the proper frequency.

E. Action

1. Aqueous LCS

a. If the LCS recovery for any analyte falls within the range of 50-79% or >120%, qualify positive results as estimated ("J").

b. If results are below the reporting limit and the LCS recovery is greater than 120%, the data are acceptable.

c. If results are less than the reporting limit and the LCS recovery falls within the range of 50-79%, qualify the data for these samples as estimated ("UJ").

d. If LCS recovery results are <50%, qualify the data for these samples as unusable ("R").

2. Solid LCS

a. If the solid LCS recovery for any analyte falls outside the EPA control limits, qualify all sample positive results as estimated ("J").

b. If the LCS results are higher than the control limits and the sample results are below the reporting limit, the data are acceptable.

c. If the LCS results are lower than the control limits, qualify all sample results below the reporting limit as estimated ("UJ").

VII. DUPLICATE SAMPLE ANALYSIS

A. Review Items

Duplicate Summaries (Form VIs) and raw data

B. Objective

Duplicate analyses are indicators of the precision of the sample results.

C. Criteria:

1. Samples identified as field or equipment blanks can not be used for duplicate sample analysis.

2. A control limit of 20% (35% for solids) for the relative percent difference (RPD) shall be used for sample values ≥5 times the reporting limit.

3. A control limit of ± reporting limit (±2× reporting limit for solids) shall be used for sample values less than 5 times the reporting limit, including the case when only one sample value is <5× reporting limit or when one sample is above the reporting limit and one is "not-detected".

4. A duplicate sample must be prepared and analyzed for every 20 samples, for every batch digested, or for every matrix, whichever is more frequent.

D. Evaluation Procedure

1. Review Form VI and verify that results fall within the control limits.

2. Check the raw data and recalculate one or more RPD to verify that results have been correctly reported on the Form VI.

3. Verify that the field blank was not used for duplicate analysis.

4. Verify that duplicates were prepared at the required frequency.

E. Action

1. If duplicate analysis results for a particular analyte fall outside the appropriate control windows, qualify the results for that analyte in all samples of the same matrix as estimated ("J").

2. If the field blank was used for duplicate analysis, all other QC data must be carefully checked and professional judgment exercised when evaluating the data.

VIII. MATRIX SPIKE/MATRIX SPIKE DUPLICATES

A. Review Items

Matrix Spike Summaries (Form V's) and raw data

B. Objective

The matrix spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology.

C. Criteria

1. Samples identified as field or equipment blanks cannot be used for spike sample analysis.

2. Spike recovery (%R) must be within the limits of 80-120%. However, spike recovery limits do not apply when sample concentration exceeds the spike concentration by a factor of 4 or more.

3. If the matrix spike recovery does not meet criteria, a post-digestion spike is required and reported on Form VB for ICP, furnace, mercury, and cyanide.

D. Evaluation Procedure

1. Review Form V's and verify that results fall within the specified limits.

2. Check raw data and recalculate one or more %R to verify that the results were correctly reported on Form V's.

3. Verify that the field blank was not used for spike analysis.

4. Verify that a matrix spike was prepared at the proper frequency.

5. Verify that a post-digestion spike was performed for all analytes with unacceptable pre-digestion spike recovery.

E. Action

1. If the spike recovery is >120% and the reported sample results are below the reporting limit, the data is acceptable for use.

2. If the spike recovery is >120% or <80% and the reported sample levels are above the reporting limit, qualify the data for these samples as estimated ("J").

3. If the spike recovery falls within the range of 30-80% and the sample results are less than the reporting limit, qualify the data for these samples as estimated ("UJ").

4. If the spike recovery results fall <30% and the sample results are less than the reporting limit, qualify the data for these samples as unusable ("R").

5. If the field blank was used for matrix spike analysis, all other QC data must be carefully checked and professional judgment exercised when evaluating the data.

IX. FURNACE ATOMIC ABSORPTION ANALYSIS

A. Review Items

Form I's and raw data

B. Objective

Duplicate injections and furnace post digestion spikes establish the precision and accuracy of the individual analytical determinations.

C. Criteria

1. For sample concentrations above the reporting limit, duplicate injections must agree within ±20% relative standard deviation (RSD) or coefficient of variance (CV), otherwise the sample must be rerun once (two additional injections).

2. Spike recovery must be ≥85% and ≤115%.

3. If post-digestion spike recovery is not within 85-115% and sample absorbance is >50% of spike absorbance, the method of standard addition is required. The sample must be spike with standards at 50, 100, and 150% of the sample absorbance.

D. Evaluation Procedure

1. Check the raw data to verify that duplicate injections were performed and agree within ±20% RSD or CV for sample concentrations above the reporting limit.

2. Review furnace raw data for verify that the furnace AA scheme as described in the CLP SOW has been followed.

3. Verify the percent recoveries were calculated correctly.

4. Verify that all required MSA results are reported on Form VIII's and check that the correlation coefficients and sample results are calculated correctly.

E. Action

1. If duplicate injections are outside the ± 20%RSD or CV limits and the sample has not been rerun once as required, qualify the data as estimated ("J").

2. If the rerun sample results do not agree within ± 20% RSD or CV, qualify the data as estimated ("J").

3. If the post digestion spike recovery is <40%, qualify results below the reporting limit as estimated ("UJ").

4. If the post-digestion spike recovery is <40%, qualify positive results as estimated ("J").

5. If the post-digestion spike recovery is <10%, qualify "not-detected" results as unusable ("R").

6. If sample absorbance is <50% of the post-digestion spike absorbance then:

a. For positive sample results less than the reporting limit, if the furnace post-digestion spike recovery is not within 85-115%, qualify the data for these samples as estimated ("J").

b. For sample results less than the reporting limit, if the furnace post-digestion spike recovery is not within 85-115%, qualify the data for these samples results as estimated ("UJ").

7. If MSA is required but has not been done, qualify the data as estimated ("J").

8. If any samples run by MSA have not been spiked at the appropriate levels, qualify the data as estimated ("J").

9. If the MSA correlation coefficient is <0.995, qualify the data as estimated ("J").

X. ICP SERIAL DILUTION ANALYSIS

A. Review Items

ICP Serial Dilution Summaries (Form IXs) and raw data

B. Objective

Serial dilution analysis determines whether significant physical or chemical interferences exist due to sample matrix.

C. Criteria

1. If the analyte concentration is sufficiently high (concentration in the original sample is minimally a factor of 50 above the reporting limit), the laboratory is required to report the results of a five fold dilution. Results that do not agree within 10% of the original results are flagged with "E" by the laboratory.

2. A serial dilution is required for each matrix analyzed.

D. Evaluation Procedure

1. Verify that reported results for the serial dilution meet required criteria of ±10%D.

2. Check the raw data and recalculate the %D to verify that the dilution analysis results agree with initial sample results reported on the Form IXs.

3. Check the raw data for evidence of negative interference, i.e., results of the undiluted samples are significantly higher than the original sample.

E. Action

1. When specified criteria are not met, qualify the associated data as estimated ("J").

2. If evidence of negative interference is found, use professional judgment to qualify the data.

XI. SAMPLE RESULT VERIFICATION

A. Review Items

Form I's and raw data

B. Objective

To ensure that the reported quantitation results are accurate.

C. Criteria

Analyte quantitation must be calculated in accordance with the appropriate SW-846 Method.

D. Evaluation Procedure

The raw data should be examined to verify the correct calculation of sample results reported by the laboratory. Digestion and distillation logs, instrument printouts, strip charts, etc., should be compared to the reported results on the Form I's.

1. Examine the raw data for any anomalies (i.e., baseline shifts, negative absorbance, omissions, legibility, etc.).

2. Verify that there are no transcription or reduction errors (e.g. dilutions, percent solids, sample weights).

3. Verify that results fall within the linear range of the ICP and within the calibrated range for the non-ICP parameters.

E. Action

If there are any discrepancies found, the laboratory may be contacted to obtain additional information that could resolve differences. If a discrepancy remains unresolved, the reviewer may determine qualification of the data is warranted.

XII. FIELD DUPLICATES

A. Review Items

Form I's and raw data

B. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

C. Criteria

There are no specific review criteria for field duplicate analyses comparability.

D. Evaluation Procedure

Samples which are field duplicates should be identified. The reviewer should compare the results reported for each sample and duplicate and calculate the relative percent difference (RPD).

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met:

1. A control limit of 20% (40% for solids) for the RPD shall be used for sample values greater than or equal to 5× the reporting limit.

2. A control limit if ± 2× the reporting limit (±4× the reporting limit for solids) shall be used for sample values less than 5× the reporting limit.

XIII. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results and, if available, Quality Assurance Project Plan and Field Sampling Plan

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation Procedure

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data.
   - Review all available information, including the Quality Assurance Project

Plan, Field Sampling Plan and communication with the data user that concerns the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his assessment of the usability of the data within the given context.

XIV. AUTHORITY

This data validation SOP for the analysis for cyanide, mercury, and metals by SW-846 methodology has been prepared by Environmental Standards, Inc. for the 3M Corporation Cordova projects. This SOP is not to be used for any other project or by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date: _____

Rock J. Vitale, CPC
Director of Chemistry

STANDARD OPERATING PROCEDURES FOR DATA VALIDATION

OF TITRIMETRIC METHODS*

(MCAWW METHODS 130.2, 305.1, 310.1, 320.1, 325.3, 330.1, 330.2, 330.3, 330.4, 335.1, 335.2, 345.1, 376.1, 377.1, 410.1, 410.2, AND 410.3 and SW-846 METHODS 9030A, 9252A, AND 9253)

I. METHOD SUMMARY

The titrimetric analysis examined in this SOP are used to determine the concentration of various wet chemistry parameters in aqueous samples. Generally, for titrimetric methods, a controlled amount of titrant (standard solution of known concentration) is added to a volume of prepared sample in the presence of an indicator compound. A change in the color of the solution signals that the amount of analyte in the sample is equivalent to the amount of the standard compound in the titrant (in some cases, a pH meter or amperometer is used to detect the equivalence point). When the equivalence point is reached, the concentration of the analyte can be determined from the volume and concentration of the titrant. The following is a list of analytes commonly determined using titrimetric methods, the titrant used, and the indicator.

Analyte	Method #	Titrant	Indicator
Hardness (Total)	MCAWW 130.2	monomagnesium ethylenediamine-tetraacetate	Calgamite or Eriochrome Black T
Acidity	MCAWW 305.1	sodium hydroxide, 0.02N	pH 8.2
Alkalinity	MCAWW 310.1	sulfuric or hydrochloric acid, 0.1N or 0.02N	pH 4.5
Bromide	MCAWW 320.1	phenylarsine oxide or sodium thiosulfate	starch indicator

* See Section IX for Authority and Application of this SOP.

Analyte	Method #	Titrant	Indicator
Chloride	MCAWW 325.3	mercuric nitrate	diphenylcarbazone-bromophenol blue
Chloride	SW-846 9252A	mercuric nitrate	diphenylcarbazone-bromophenol blue
Chloride	SW-846 9253	silver nitrate	potassium chromate
Chlorine (Total Residual)	MCAWW 330.1	phenylarsine oxide or sodium thiosulfate	amperometer
Chlorine (Total Residual)	MCAWW 330.2	standard iodine titrant (0.0282N)	starch indicator or amperometer
Chlorine (Total Residual)	MCAWW 330.3	phenylarsine oxide or sodium thiosulfate	starch indicator
Chlorine (Total Residual)	MCAWW 330.4	standard ferrous ammonium sulfate	*N,N*-diethyl-*p*-phenylenediamine
Cyanides (Amenable to Chlorination)	MCAWW 335.1	silver nitrate	*p*-dimethylamino-benzal-rhodamine
Cyanide (Total)	MCAWW 335.2	silver nitrate	*p*-dimethylamino-benzal-rhodamine
Iodide	MCAWW 345.1	phenylarsine oxide or sodium thiosulfate	starch indicator
Sulfide	MCAWW 376.1	phenylarsine oxide or sodium thiosulfate	starch indicator
Sulfide	SW-846 9030A	phenylarsine oxide or sodium thiosulfate	starch indicator
Sulfite	MCAWW 377.1	standard potassium iodide-iodate	starch indicator
Chemical Oxygen Demand	MCAWW 410.1	standard ferrous ammonium sulfate	orthophenanthroline ferrous complex
Chemical Oxygen Demand (Low Level)	MCAWW 410.2	standard ferrous ammonium sulfate	orthophenanthroline ferrous complex
Chemical Oxygen Demand (High Level)	MCAWW 410.3	standard ferrous ammonium sulfate	orthophenanthroline ferrous complex

II. TECHNICAL HOLDING TIMES

A. Review Items

Analytical result pages, Chain-of-Custody forms, raw data, and Case Narrative

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of analysis.

C. Criteria

Technical requirements for sample holding times are based on the project-specific QAPP. The following holding times are based on the specific methods.

Parameter	Preservative[1]	Holding Time[2]
Hardness	HNO_3 to pH < 2	6 Months
Acidity	Cool, 4±2°C	14 Days
Alkalinity	Cool, 4±2°C	14 Days
Bromide	None Required	28 Days
Chloride	None Required	28 Days
Chlorine	None Required	Analyze Immediately[3]
Cyanide	Cool, 4±2°C, NaOH to pH >12	14 Days
Iodide	Cool, 4°C	24 Hours
Sulfide	Cool, 4±2°C, add 2mL zinc acetate plus NaOH to pH > 9	7 Days
Sulfite	None Required	Analyze Immediately[3]
COD	Cool, 4±2°C, H_2SO_4 to pH <2	28 Days

1 Sample preservation should be performed immediately upon sample collection.
2 From sample collection to sample analysis.
3 For data validation purposes, a 24-hour holding time will be used for chlorine and sulfite.

D. Evaluation

Technical holding times are established by comparing the sampling dates on the Chain-of-Custody forms with the dates of analysis on the Form I's and the raw data.

E. Action

1. If the analysis of aqueous samples was performed between the end of the holding time up to twice the holding time after the sample collection, flag all positive results as estimated "J" and all "not-detected" results "UJ".

2. If the analysis of aqueous samples was performed greater than twice the holding time after the date of sample collection, the analysis for target analytes in all samples should be considered unreliable; positive results should be qualified as estimated ("J"); and the "not-detected" results should be flagged "R".

3. Note the holding time exceedance in the QA report.

4. If the temperature of samples upon receipt at the laboratory exceeds 10°C, attempt to ascertain how the temperature was obtained. If the temperature was obtained from a temperature bottle or an IR gun and the temperature is greater than 10°C, qualify positive results as estimated ("J") and "not-detected" results as "UJ".

5. If documentation of the chemical preservation of samples was not provided by the laboratory, contact the laboratory and request the information. If it can be documented that chemical preservation of the samples was <u>not</u> performed, or if the pH of the samples upon receipt at the laboratory did not meet the preservation requirements, qualify all positive results for analytes requiring chemical preservation as estimated ("J") and all "not-detected" results "UJ".

III. INITIAL AND CONTINUING CALIBRATIONS

A. Review Items

Analytical result pages and raw data

B. Objective

The objective of initial calibrations is to ascertain that the titrant used in the analysis has been standardized (to confirm and document an exact concentration) and, if a pH meter or amperometer is used, to demonstrate adequate performance of the pH meter or amperometer. The methods provided in the QAPP and laboratory analytical SOPs may provide criteria for initial and continuing calibrations which differ from the criteria specified below. Refer to the site-specific documents for the requirements stipulated for the project.

C. Criteria

1. Each titrant must be standardized prior to sample analysis to calculate an exact concentration of the titrant. This concentration is used in the calculation of the sample results.

2. For amperometric or pH determinations of endpoints, the laboratory must analyze at least two standard reference solutions at concentrations which bracket the endpoint prior to analysis of the samples.

3. For amperometric or pH determinations of endpoints, the laboratory must analyze a standard reference material (preferably at a concentration near the endpoint of the analysis) every 10 samples and at the end of the analytical run to demonstrate that instrumental drift has not occurred.

D. Evaluation

1. Verify that the laboratory standardized all titrants prior to use and that the calculation of the titrant concentration was performed correctly. In addition, verify that the laboratory used the standardization concentration to calculate the positive results for the project samples.

2. Verify that the laboratory analyzed at least two standard reference solutions prior to sample analysis to demonstrate acceptable instrument responses (if the endpoint for the analysis was determined using a pH meter or an amperometer). The results obtained from the standard reference solutions should be within 10% of the true value for the solutions.

3. For amperometric or pH determination of the endpoint, verify that the laboratory analyzed a standard reference solution after every 10 project samples and at the end of the analytical run. To demonstrate acceptable performance, the results obtained must be within 10% of the true value for the standard reference material. If unacceptable recoveries are obtained, the laboratory should have terminated the analysis, recalibrated the instrument, and reanalyzed all samples analyzed since the last acceptable continuing calibration.

E. Action

1. If the laboratory did not provide documentation of the initial and/or continuing calibrations or of the standardization of the titrant, contact the laboratory and request the missing information.

2. If the laboratory did not standardize the titrant prior to analysis, qualify all positive results as estimated ("J") and flag all "not-detected" results "UJ". However, professional judgment should be used to determine if the analysis should be considered unusable.

3. If unacceptable results (outside 90-110% of the true value) were observed for the initial and/or continuing calibrations and the laboratory did not recalibrate the instrument and reanalyze all associated samples, qualify all positive results as estimated ("J") and flag all "not-detected" results "UJ". However, use professional judgment to determine if the analysis should be considered unusable. In general, if the initial or continuing calibration analyses display recoveries outside 75-125%, then the analysis should be considered unusable (flag all positive results and detection limits "R").

4. Use professional judgment to determine if data should be qualified in the even that the laboratory analyzes only one standard reference solution for the initial calibration of the amperometer or pH meter (as opposed to two or three solutions).

IV. BLANKS

A. Review Items

QC summary forms and raw data

B. Objective

The assessment of blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting other data.

C. Criteria

The methods give little to no criteria for method (distilled water) blank analyses or corrective action for positive results reported for the method and calibration blanks except for the methods listed below. Refer to the project-specific QAPP for quality control criteria and corrective actions for the method blanks without specific guidance from the methods.

Parameter / Method	Type of Blank	Criteria
Bromide / MCAWW Method 320.1	distilled water	A distilled water blank must be run with each set of samples because of iodide, iodate, bromide, and/or bromate in reagents.
Chloride / SW-846 Method 9252A	reagent water	Employ a minimum of one blank per analytical batch or twenty samples, whichever is more frequent.
Chloride / SW-846 Method 9253	reagent water	Employ a minimum of one blank per analytical batch or twenty samples, whichever is more frequent.
Iodide / MCAWW Method 345.1	distilled water	A distilled water blank must be run with each set of samples because of iodide in reagents.
Sulfite / MCAWW Method 377.1	distilled water	A blank must be run to correct for interferences present in the reagents.

Parameter / Method	Type of Blank	Criteria
COD / MCAWW Method 410.1	distilled water low in COD	A blank is analyzed simultaneously as the samples following the details in the method, but using low COD water in place of sample.
COD / MCAWW Method 410.2	distilled water low in COD	A blank is analyzed simultaneously as the samples following the details in the method, but using low COD water in place of sample.
COD / MCAWW Method 410.3	distilled water	A blank is analyzed using 50 mL of distilled water in place of the sample together with all reagents and subsequent treatment.

The following criteria will be used to assess data quality.

1. A method blank (reagent water carried through all sample preparation and analysis steps) shall be prepared at a frequency of one per twenty samples or with every batch of samples digested, whichever is more frequent.

2. The method blank shall not display positive results for the analyte greater than the reporting limit. If the method blank displays a positive result greater than the reporting limit, the laboratory shall reprepare and reanalyze all associated samples.

3. A field and/or equipment blank shall be collected at the frequency of one per twenty field samples, or per the frequency stated in the project-specific QAPP.

4. The field and/or equipment blanks shall not display levels of the analytes at levels greater than the reporting limit.

5. The laboratory shall not blank-subtract any positive result reported for the analysis.

D. Evaluation

1. Verify the reported results against the strip-chart recordings and/or notebook pages to determine consistency and to determine if these blanks have acceptable analytical results.

2. Verify that every sample within the data set has an associated method blank.

3. Verify that each method blank does not contain the target analyte in excess of the reporting limit.

4. Verify there is a field and/or equipment blank for every data set of 20 samples or less (or per the frequency stated in the project-specific QAPP).

5. Verify that the field and/or equipment blanks do not contain target analytes above the reporting limit.

E. Action

1. Any missing items, inconsistencies or errors must be resolved by the laboratory.

2. If the laboratory has utilized blank subtraction, the laboratory must resubmit the data unsubtracted. It should be noted that a reagent blank is used to assess the initial amount of titrant necessary to reach the end point in pure water. This volume is subtracted from the amount necessary to reach the end point for a sample. However, this is <u>not</u> considered blank-subtraction.

3. If a field and/or equipment blank is not present, note this in the QA report.

4. If the target analyte is present in any blank above the reporting limit, the following apply:

   a. If the target analyte is detected in any blank, all results for associated samples which are less than five times the blank concentration are qualitatively questionable and are qualified "U" on the data summary table.

   b. If the result for the target analyte in any sample is greater than five times the blank result, do not flag the result, but note the level detected.

V. MATRIX SPIKES/MATRIX SPIKE DUPLICATES, BLANK SPIKES, OR LABORATORY CONTROL SAMPLES

A. Review Items

QC summary forms, chromatograms, and integration reports

B. Objective

Data for matrix spikes (MS)/matrix spike duplicates (MSD) are generated to determine long-term accuracy and precision of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data are used to evaluate the accuracy of other samples in the specified batch of analytical samples. The data for blank spikes (BS) or laboratory control samples (LCS) are generated to determine analytical accuracy. The results of blank spikes are used to assess accuracy of the entire sample batch.

C. Criteria

The analytical methods do not provide recovery criteria for MS/MSDs, BS or LCS analyses, or relative percent difference (RPD) criteria for comparing MS/MSD results. See the project-specific QAPP for contract-required recoveries/RPDs and corrective action. For the purposes of data validation, a recovery range of 75-125% shall be used for MS/MSDs and a recovery range of 80-120% shall be used for BS and LCS analyses. In addition, an RPD upper limit of 20% shall be used for comparing MS/MSD results.

D. Evaluation

1. Verify that an MS or MS/MSD was performed one in 20 samples and a BS or LCS was performed one in 20 samples.

2. Verify that there is consistency between the raw data and the recoveries reported.

3. Verify that the MS/MSD recoveries were within the range of 75 to 125% and the BS/LCS recoveries were within 80 to 120%.

4. Verify that the RPD between the results for target analytes in the MS/MSD analysis is less than 20%.

5. Verify that matrix spikes were not performed on field or rinse blanks.

E. Action

1. Any inconsistencies/errors must be resolved by the laboratory.

2. If an MS (or MSD) and an LCS (or BS) was not performed, note this fact in the QA report.

3. If the MS (or MSD) was performed on a designated field or rinse blank, note the deficiency in the QA report.

4. If the recoveries are outside criteria, the following apply:

Matrix Spikes/Matrix Spike Duplicates

a. %R < 75% but > 30% : flag positive results as estimated ("J") and "not-detected" results "UJ".

b. %R < 30%: flag positive results as estimated ("J") and "not-detected results as unreliable ("R").

c. %R > 125%: flag positive results as estimated ("J"). Qualification of "not-detected" results is not necessarily required based on this issues alone.

Blank Spikes/Laboratory Control Samples

a. %R < 80% but > 50%: flag positive results as estimated ("J") and "not-detected results as unreliable ("UJ").

b. %R < 50%: flag positive results as estimated ("J") and "not-detected results as unreliable ("R").

c. %R > 120% but < 150%: flag positive results as estimated ("J"). Qualification of "not-detected" results is not required .

In all situations above, the validation report must indicate the direction and severity of the bias.

VI. FIELD DUPLICATES

A. Review Items

Form I and raw data

B. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates, which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

C. Criteria

There are no specific review criteria for field duplicate analyses comparability; however, validation criteria are specified below. Refer to QAPP for project-specific requirements concerning frequency of collection of field duplicates and the precision necessary for the data quality objectives.

D. Evaluation

Samples which are field duplicates should be identified. Check the Chain-of-Custody Records or contact the client for field duplicate information. The reviewer should compare the results reported for each sample and duplicate and calculate the relative percent difference (RPD) for the field duplicate pair.

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met.

1. A control limit of ±20% for aqueous samples (±40% for solid samples) for the RPD shall if both the initial sample and field duplicate sample display results greater than 5× the reporting limit.

2. A control limit of ± the reporting limit (±2× the reporting limit for solid samples) shall be used for all samples if either one or both of the initial and field duplicate sample results were less than 5× the reporting limit.

VII. SAMPLE RESULT VERIFICATION

A. Review Items

All Analytical Summary Forms, raw data, and sample preparation logs

B. Objective

As part of the data validation effort, all positive results for target analytes in the samples must be verified through recalculation from the raw data result to the final results reported on the Analytical Summary Forms. In addition, all "not-detected" results must be verified against the raw data.

C. Criteria

The laboratory must provide all raw data necessary to recalculate all results reported (both positive and "not-detected" results). All results must be calculated as per the method and include any dilution factors and differences in the sample volume used (as opposed to the volume required by the method).

D. Evaluation

1. Verify that all required data is present. Verify that all laboratory calculations are present for all positive sample results and QC sample results.
2. Recalculate 100% of the positive sample results.

3. Verify that the reported reporting limit is achievable based on the raw data and the results for the quality control analyses.

E. Action

1. Any data that is incorrect and/or missing (i.e., sample calculations) must be resolved/submitted by the laboratory.

2. Reviewer's professional judgment should be used to evaluate whether the reported detection limits were achieved. If qualification of data is necessary, full documentation and an explanation must be provided in the validation report.

3. If a positive result has been reported incorrectly due to a calculation error, address the issue in the QA report.

VIII. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results, QAPP, and Field Sampling Plan

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the client in avoiding inappropriate use of the data. Review all available information, including the QAPP, Field Sampling Plan, and communications with the client that concerns the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Prepare a fully documented quality assurance review which provides the client with an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his assessment of the usability of the data within the given context.

IX. AUTHORITY

This data validation SOP for the analysis of titrimetric methods has been prepared by Environmental Standards, Inc. for the 3M Corporation Cordova projects. This SOP is not to be used for any other project or by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date:_____

Rock J. Vitale, CPC
Director of Chemistry

STANDARD OPERATING PROCEDURES FOR DATA VALIDATION OF ION SELECTIVE ELECTRODE METHODS*

(METHODS 351.4, 340.2, AND 350.3)

I. METHOD SUMMARY

This Standard Operating Procedure concerns the validation of data generated by the analysis of aqueous samples for wet chemistry parameters using ion-selective electrodes. The target parameters are determined potentiometrically using an electrode and a pH meter having an expanded millivolt scale or a selective ion meter. Raw data for these analyses include an analysis run log (usually with results and sample numbers entered by hand) and/or a strip-chart printout of the pH meter. It should be noted that these methods do not provide guidance to the analyst for quality assurance analyses (type, frequency, acceptability, or corrective actions). In addition, the criteria specified in this SOP may differ from those stated in site-specific Quality Assurance Project Plans (QAPPs) and laboratory analysis SOPs. Therefore, some of the sections in this SOP might not be directly applicable to all situations.

II. TECHNICAL HOLDING TIMES

A. Review Items

Analytical result pages, Chain-of-Custody Records, raw data, and Case Narrative

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of analysis.

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* **See Section X for Authority and Application of this SOP.**

C. Criteria

Technical requirements for sample holding times are based on the project-specific QAPP. The holding time criteria is listed below according to the Methods for Chemical Analysis of Water and Waste and is from the date of sample collection to the date of sample analysis.

Parameter / Method	Preservative	Holding time
Fluoride / MCAWW 340.2	None Required	28 Days
Nitrogen - Ammonia / MCAWW 350.3	Cool, 4° C, H_2SO_4 to pH <2	28 Days
Total Kjeldahl Nitrogen / MCAWW 351.4	Cool, 4° C, H_2SO_4 to pH <2	28 Days

D. Evaluation

Technical holding times are established by comparing the sampling dates on the Chain-of-Custody forms with the dates of analysis on the Analysis Results summaries (Form I's) and the raw data.

E. Action

1. If the analysis of aqueous samples was performed between 28 and 56 days after the sample collection, flag all positive results as estimated ("J") and all "not-detected" results ("UJ").

2. If the analysis of aqueous samples was performed greater than 56 days beyond the date of sample collection, the target analyte should be considered unreliable; the positive results should be qualified as estimated values ("J"), and the "not-detected" results should be flagged "R."

3. Note the holding time exceedance in the QA report.

4. If the temperature of samples upon receipt at the laboratory exceeds 10°C, attempt to ascertain how the temperature was obtained. If the temperature was obtained from a temperature bottle or an IR gun and the temperature is

greater than 10°C, qualify positive values as estimated ("J") and "not-detected" results as "UJ". Include this deficiency in the quality assurance report.

5. If pH adjustment was required for the preservation of the sample for a particular analysis but the chemical preservation was not added to the sample, include this deficiency in the quality assurance report. In addition, flag all positive results as estimated ("J") and all "not-detected" results "UJ".

III. INITIAL CALIBRATION

A. Review Items

Calibration summary forms, integration reports, and chromatograms

B. Objective

Requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for the target parameter compounds.

C. Criteria

Initial calibration standards containing the target analytes are analyzed at several concentrations (over the linear range) at the beginning of each analytical sequence or as necessary if the continuing calibration acceptance criteria are not met. See the specific methods (laboratory SOPs) for suggestions on standards volumes, etc.

D. Evaluation

1. Verify that the correct number of standards were used for the initial calibration.

2. Verify that the correct initial calibration curve was used for all sample quantitations.

3. For the fluoride analysis, verify that the slope of the calibration curve is between -54 and -59 (inclusive).

E. Action

1. If the initial calibration was not performed in the appropriate manner (as stated above) or at the required frequency, a noncorrectable deficiency must be included in the quality assurance review. In addition, use professional judgment to determine if data should be qualified due to this deficiency.

2. If the laboratory used a straight-line (first-order) equation for the calibration curve and the correlation coefficient for the curve was less than 0.995, flag all positive results "J". Flag detection limits in severe cases (consult the Data Validation Task Manager).

IV. CONTINUING CALIBRATIONS

A. Review Items

QC Summary forms and raw data

B. Objective

Continuing calibrations are used to demonstrate acceptable instrument stability and performance throughout the period of time during which samples are analyzed. Instrument drift or analytical problems, which may have an adverse effect on the analytical results, are demonstrated by poor results for the continuing calibration analyses.

C. Criteria

1. The continuing calibration verification (CCV) is performed at the beginning and end of the analytical run and after every 10 samples analyzed.

2. The CCV must display results within 90-110% of the true value. Otherwise, the laboratory must terminate the analysis, recalibrate the instrument, and reanalyze all samples analyzed since the last compliant CCV.

D. Evaluation

1. Review the raw data recordings and/or notebook pages to verify consistency between dates and times and between raw data and QC forms.

2. Verify that the CCVs were performed at a minimum of once every 10 samples and before and after all samples were analyzed.

3. Verify that the recoveries for the CCVs were within 90-110% of the true value of the CCV standard.

E. Action

1. Any inconsistencies/errors must be resolved by the laboratory. Analytical results should be considered tentative until the laboratory resolves these issues.

2. For CCV results outside 90-110%, positive results for associated samples should be considered estimated (flagged "J").

3. If the CCV displays results less than 90%, flag "not-detected" results "UJ".

4. If the CCV displays results less than 75%, flag all positive and "not-detected" results as unusable ("R").

5. If the CCV recovery exceeds 125%, flag all positive results as unusable ("R"). "Not-detected" results are acceptable as reported.

V. BLANKS

A. Review Items

QC summary forms and raw data

B. Objective

The assessment of blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for the evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting other data. Refer to the QAPP for project-specific criteria for field and/or equipment blanks.

C. Criteria

The method gives no criteria for method (distilled water) blank analyses or corrective action for positive results reported for the method and calibration blanks. Refer to the project-specific QAPP for quality control criteria and corrective actions for the method blanks without specific guidance from the QAPP. The following criteria will be used to assess data quality:

1. A method blank (reagent water carried through all sample preparation and analysis steps) shall be prepared at a frequency of one per 20 samples or with every batch of samples prepared, whichever is more frequent.

2. The method blank shall not display positive results for the analyte greater than the reporting limit. If the method blank displays a positive result greater than the reporting limit, the laboratory shall reprepare and reanalyze all associated samples.

3. A field and/or equipment blank shall be collected at a frequency of one per 20 field samples, or per the frequency stated in the project-specific QAPP.

4. The field and/or equipment blanks shall not display levels of the analytes at levels greater than the reporting limit.

5. The laboratory shall not blank-subtract any positive result reported for the analysis.

D. Evaluation

1. Verify the reported results against the strip-chart recordings and/or notebook pages to determine consistency and to determine if these blanks have acceptable analytical results.

2. Verify that every sample within the data set has an associated method blank.

3. Verify that each method blank does not contain target analytes in excess of the reporting limit.

4. Verify that there is a field and/or equipment blank for every data set of 20 samples or less (or per the frequency stated in the project-specific QAPP).

5. Verify that the field and/or equipment blanks do not contain target analytes above the reporting limit.

6. Verify that the laboratory did not blank-subtract analytical results.

E. Action

1. Any missing items, inconsistencies, or errors must be resolved by the laboratory.

2. If the laboratory has utilized blank subtraction, the laboratory must resubmit the data unsubtracted.

3. If a field and/or equipment blank is not present, note this in the QA report.

4. If the target parameter is present in any blank above the reporting limit, the following apply:

   a. If the target parameter is detected in any blank, all results for associated samples which are less than five times the blank concentration are qualitatively questionable and are qualified "U" on the data summary table.

b. If the result for the target parameter in any sample is greater than five times the blank result, do not flag the result, but note the level detected.

VI. MATRIX SPIKES/MATRIX SPIKE DUPLICATES, BLANK SPIKES, OR LABORATORY CONTROL SAMPLES

A. Review Items

QC summary forms and raw data

B. Objective

Data for matrix spikes (MS)/matrix spike duplicates (MSD) are generated to determine long-term accuracy and precision of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data are used to evaluate the accuracy of other samples in the specified batch of analytical samples. The data for blank spikes (BS) or laboratory control samples (LCS) are generated to determine analytical accuracy. The results of blank spikes are used to assess accuracy of the entire sample batch.

C. Criteria

The analytical method does not provide recovery criteria for MS/MSDs, BS, or LCS analyses or relative percent difference (RPD) criteria for comparing MS/MSD results. See the project-specific QAPP (and laboratory analysis SOPs) for contract-required recoveries/RPDs and corrective action. For the purposes of data validation, a recovery range of 75-125% shall be used for MS/MSDs and a recovery range of 80-120% shall be used for BS and LCS analyses. In addition, an RPD upper limit of 20% (aqueous) and 40% (solids) shall be used for comparing MS/MSD results.

D. Evaluation

1. Verify that an MS or MS/MSD was performed one in 20 samples and a BS or LCS was performed one in 20 samples.

2. Verify that there is consistency between the raw data and the recoveries reported.

3. Verify that the MS/MSD recoveries were within the range of 75-125% and the BS/LCS recoveries were within 80-120%.

4. Verify that the RPD between the results for the target analyte in the MS/MSD analysis is less than 20% (aqueous) and 40% (solids).

5. Verify that matrix spikes were not performed on field or rinse blanks.

E. Action

1. Any inconsistencies/errors must be resolved by the laboratory.

2. If an MS (or MSD) and an LCS (or BS) were not performed, note this fact in the QA report.

3. If the MS (or MSD) was performed on a designated field or rinse blank, note the deficiency in the QA report.

4. If the recoveries are outside criteria, the following apply:

Matrix Spikes/Matrix Spike Duplicates

a. %R < 75% but > 30% : flag positive results as estimated ("J") and "not-detected" results "UJ."
b. %R < 30%: flag positive results as estimated ("J") and "not-detected results as unreliable ("R").
c. %R > 125%: flag positive results as estimated ("J"). Qualification of "not-detected" results is not necessarily required based on this issue alone.
d. %RPD > 20% (aqueous) or 40% (solids): flag positive results as estimated ("J"). Qualification of "not-detected" results is not necessarily required based on this issue alone.

Blank Spikes/Laboratory Control Samples

a. %R < 80% but > 50%: flag positive results as estimated ("J") and "not-detected results as unreliable ("UJ").

b. %R < 50%: flag positive results as estimated ("J") and "not-detected results as unreliable ("R").

c. %R > 120% but < 150%: flag positive results as estimated ("J"). Qualification of "not-detected" results is not required .

d. %RPD > 20% (aqueous) or 40% (solids): flag positive results as estimated ("J"). Qualification of "not-detected" results is not necessarily required based on this issue alone.

In all situations above, the validation report must indicate the direction and severity of the bias.

VII. FIELD DUPLICATES

A. Review Items

Form I and raw data

B. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates, which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

C. Criteria

There are no specific review criteria for field duplicate analyses comparability; however, validation criteria are specified below. Refer to QAPP for project-specific requirements concerning frequency of collection of field duplicates and the precision necessary for the data quality objectives.

D. Evaluation

Samples which are field duplicates should be identified. Check the Chain-of-Custody Records or contact the client for field duplicate information. The reviewer should compare the results reported for each sample and duplicate and calculate the relative percent difference (RPD) for the field duplicate pair.

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met.

1. A control limit of ±20% for aqueous samples (±40% for solid samples) for the RPD shall if both the initial sample and field duplicate sample display results greater than 5× the reporting limit.

2. A control limit of ± the reporting limit (±2× the reporting limit for solid samples) shall be used for all samples if either one or both of the initial and field duplicate sample results were less than 5× the reporting limit.

VIII. SAMPLE RESULT VERIFICATION

A. Review Items

All Analytical Summary Forms, raw data, and sample preparation logs

B. Objective

As part of the data validation effort, all positive results for the target parameters in the samples must be verified through recalculation from the raw data result to the final results reported on the Analytical Summary Forms. In addition, all "not-detected" results must be verified against the raw data.

C. Criteria

The laboratory must provide all raw data necessary to recalculate all results reported (both positive and "not-detected" results). All results must be calculated as per the

method and include any dilution factors and differences in sample volume used (as opposed to the volume required by the method).

D. Evaluation

1. Verify that all required data is present. Verify that all laboratory calculations are present for all positive sample results and QC sample results.

2. Recalculate 100% of the positive sample results.

3. Verify that the reported reporting limits are achievable based on the analyte signal observed for the lowest calibration standard.

4. Verify that all reported positive results were within the calibration range of the instrument.

E. Action

1. Any data that is incorrect and/or missing (i.e., sample calculations) must be resolved/submitted by the laboratory.

2. Reviewer's professional judgment should be used to evaluate whether the reported detection limits were achieved. If qualification of data is necessary, full documentation and an explanation must be provided in the validation report.

3. If a positive result has been reported incorrectly due to a calculation error, address the issue in the QA report.

4. If a positive result for an analyte was reported from an instrument level which exceeded the calibration range, note the deficiency in the QA report and qualify the positive result as estimated ("J").

IX. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results, QAPP, and Sampling and Analysis Plan

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the client in avoiding inappropriate use of the data. Review all available information, including the QAPP, Sampling and Analysis Plan, and communications with the client that concerns the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Prepare a fully documented quality assurance review which provides the client with an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, the reviewer should include his assessment of the usability of the data within the given context.

X. AUTHORITY

This data validation SOP for the analysis of ion selective electrode methods has been prepared by Environmental Standards, Inc. for use on the 3M Corporation Cordova projects. This SOP is not to be used for any other project or used by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date:_____

Rock J. Vitale, CPC
Director of Chemistry

STANDARD OPERATING PROCEDURES FOR DATA VALIDATION OF SULFATE (MCAWW METHOD 375.4 AND SW-846 METHOD 9038)*

I. METHOD SUMMARY

This method is for the analysis of sulfate in aqueous samples. Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer or spectrophotometer and compared to a calibration curve prepared from standard sulfate solutions. Suspended matter and color interfere with the analysis. Correct for these interferences by running blanks from which the barium chloride has been omitted. In addition, high levels of silica (in excess of 500 mg/L) will interfere with the analysis.

II. TECHNICAL HOLDING TIMES

A. Review Items

Analytical result form (Form I equivalent), Chain-of-Custody forms, raw data and Case Narrative

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of analysis. Analytical results for samples analyzed in excess of the specified holding time may be considered estimated values (possibly biased low) due to loss of analyte through chemical or biological activities in the sample.

C. Criteria

Technical requirements for sample holding times are based on the project-specific Quality Assurance Project Plan (QAPP). The maximum holding time for preserved samples (cooled to 4 ± 2°C) is 28 days from sample collection, as specified in the Chain-of-Custody.

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* **See Section X for Authority and Application of this SOP.**

D. Evaluation

Technical holding times are established by comparing the sampling dates on the Chain-of-Custody forms with the dates of analysis on the Form I's and the raw data. Verify that the samples were cooled to 4 ± 2°C and were analyzed within 28 days from the date of sample collection specified on the Chain-of-Custody.

E. Action

If technical holding times are exceeded, document in the quality assurance review that holding times were exceeded and qualify the sample results according to the following criteria:

1. Note the holding time exceedance in the deficiencies section of the QA report.

2. If the analysis of other aqueous samples was performed greater than one day but less than or equal to 28 days after the 28 day holding time, flag positive results as estimated ("J") and flag all "not-detected" results "UJ".

3. If the analysis of aqueous samples was performed greater than 4 days after the 28 day holding time, all "not-detected" samples results are rejected ("R"), and all positive results are qualified as estimated ("J").

4. If samples were received at temperatures greater than 10°C, qualify positive results as estimated ("J") and "not-detected" results "UJ". Professional judgment should be used to determine if the analysis should be considered unusable.

III. INITIAL CALIBRATION

A. Review Items

Raw data and initial calibration summary form

B. Objectives

The objective of the initial calibration is to demonstrate acceptable instrument levels for the analyte at various concentrations and to demonstrate linearity over a range of

concentrations of the analyte. The criteria specified below are general guidelines for assessing data quality for the sulfate analysis. See the project-specific QAPP and laboratory analysis SOP for analytical requirements.

C. Criteria

1. The laboratory must analyze, at a minimum, a blank and four standards as the initial calibration of the instrument.

2. The highest concentration standard for the initial calibration must not exceed 40 mg/L. At higher concentrations, the barium sulfate suspension becomes unstable and accuracy decreases.

3. The correlation coefficient of the initial calibration should be greater than or equal to 0.995.

4. Per SW-846, verify that the calibration curve has been performed every hour of continuous sample analysis (For MCAWW, use an 8-hour time period).

D. Evaluation

1. Verify that at least four standards and a blank were used for the initial calibration and that the correlation coefficient is at least 0.995 for linear calibration curves.

2. Verify all samples have an associated initial calibration run within a 8 hour period. (SW-846 requirement - the initial calibration must be performed every hour of continuous analysis).

3. Verify that the highest initial calibration standard did not exceed 40 mg/L sulfate.

E. Action

1. Any initial calibrations of less than four standards and a blank would not necessarily result in qualifying sample results. Use professional judgment to determine if data should be qualified if the correct number of standards was not used for the initial calibration.

2. A correlation coefficient of < 0.995 for linear calibration curves would result in qualifying all positive results as estimated ("J").

3. Any differences/inconsistencies observed in the raw data from what the laboratory has reported must be resolved by the laboratory.

4. If the laboratory used a standard in excess of 40 mg/L sulfate for the initial calibration, flag all positive results between 40 mg/L and the highest calibration standard concentration (instrument level) as estimated ("J"). Include a statement in the deficiencies section of the quality assurance review.

5. If samples are analyzed in excess of 8 hours after the initial calibration (one hour per SW-846), include a statement in the quality assurance review to this effect. However, data is not necessarily affected by this deficiency. Use professional judgment to qualify sample results. (Refer to the continuing calibration analysis results).

IV. CONTINUING CALIBRATIONS

A. Review Items

Raw data and continuing calibration summaries

B. Objective

The objective of the continuing calibrations is to demonstrate instrument stability over a period of time, thereby ensuring the accuracy of the analysis.

C. Criteria

The laboratory must analyze a continuing calibration standard every 10 samples and after all project samples have been analyzed. The continuing calibrations must display results within a range of 90-110% for acceptable continuing calibration analyses.

D. Evaluation

1. Review the strip-chart recordings and/or notebook pages to verify consistency between dates and times and consistency between raw data and QA summary forms.

2. Verify that continuing calibration standards were performed at a minimum of once after every 10 samples and at the end of the analytical run.

3. Verify that the percent recoveries were within 90%-110% of the values obtained in the initial calibration.

E. Action

1. Any inconsistencies/errors must be resolved by the laboratory. Analytical results should be considered tentative until the laboratory resolves these issues.

2. For continuing calibrations outside the 90%-110% criteria, positive results are estimated and flagged "J". If the continuing calibration displays recoveries outside 75-125%, all positive results are flagged "R" (unusable).

   Note: The continuing calibration standard should be applied to samples on both "sides" (before and after) until a compliant standard is obtained in both directions.

3. For percent recoveries less than 90% criteria for a continuing calibration standard in the direction of a sensitivity loss, negative results should be flagged "UJ". The QA report should indicate the direction of bias. If the recovery is less than 75%, the analysis should be considered unusable and the "not-detected" results should be flagged "R".

4. If continuing calibration standards were not performed at the required frequency, note the deficiency in the QA report. Use professional judgment for qualifying sample results.

5. If the laboratory reported a continuing calibration recovery which exceeded the criterion specified in the QAPP and did not reanalyze samples associated with the non-compliant continuing calibration, a statement to this effect shall be included in the deficiencies section of the quality assurance review.

V. BLANKS

A. Review Items

Blank Form I (or equivalent), Form IV (or equivalent), and raw data

B. Objective

The assessment of blank analysis results determines the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. For this method, a method blank (without the addition of barium chloride) is used to correct sample results for color. However, blank-subtracting results using a method blank which did contain barium chloride is not acceptable.

C. Criteria

1. The laboratory shall prepare and analyze one method blank (which includes the addition of barium chloride) at a frequency of one per sample batch of less than or equal to 20 samples.

2. The laboratory shall not blank subtract the results of any preparation (method) blank, field blanks, or equipment blank (all which included the addition of barium chloride) from any project sample result.

3. A continuing calibration blank shall be run immediately after each CCV.

4. All preparation (method and calibration) blanks shall not display any positive result for sulfate in excess of the reporting limit.

D. Evaluation

1. Verify the reported results against the strip-chart recordings and/or notebook pages to determine consistency and to determine if these blanks have acceptable calibrations.

2. Verify that every sample within the data set has an associated method blanks and calibration blanks.

3. Verify that each method blank and calibration blank does not contain analyte in excess of the reporting limit.

4. Verify there is a field blank for every set of samples collected on the same day and an equipment blank for each set of samples from one Solid Waste Management Unit (SWMU).

5. Verify that the field and/or equipment blanks do not contain target analytes above the reporting limit.

E. Action

1. Any missing items, inconsistencies or errors must be resolved by the laboratory. Until the laboratory clarifies/resubmits these items, the associated results are designated as tentative.

2. If the laboratory has utilized blank subtraction, the laboratory must resubmit the data unsubtracted. (A calibration blank is acceptable for defining a reference "zero" for establishing a calibration curve. In addition, the subtraction of the results for the blank which did not include barium chloride is required by the method.)

3. If method blanks were not prepared and analyzed at the required frequency, note that in the deficiency section of the quality assurance report.

4. If a field and/or equipment blank is not present, note this in the QA report.

5. If any target analyte is present in any blank above the reporting limit, the following apply:

   a. If an analyte is detected in any blank within 5 times the level in any sample, the result should be considered "not-detected" and is qualified "U" on the target summary table.

   b. If an analyte in any sample is greater than 5 times the blank result, do not flag results, but note the level in the blank in the QA report.

   c. If a method blank contains sulfate above the reporting limit, note this in the deficiency section in the quality assurance report.

VI. MATRIX SPIKES/MATRIX SPIKE DUPLICATES/BLANK SPIKES OR LABORATORY CONTROL SAMPLES

A. Review Items

Raw data, analytical results forms, and the quality control summary forms for the matrix spike/matrix spike duplicate, blank spike, and/or laboratory control samples.

B. Objective

Data for matrix spikes (MS)/matrix spike duplicates (MSD) are generated to determine long-term accuracy and precision of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. The data for blank spikes (BS) or laboratory control samples (LCS) are generated to determine analytical accuracy. The results of blank spikes are used to assess the accuracy of the entire sample batch.

C. Criteria

1. Per SW-846 Method 9038, the laboratory shall analyze a matrix spike/matrix spike duplicate sample every 10 analytical samples. No guidance for frequency of MS/MSDs is provided in MCAWW Method 375.4. Refer to the QAPP for project-specific requirements for the frequency of analysis for MS/MSD, LCS, and BS samples.

2. The methods do not specify any recovery criteria for the MS/MSD, BS, and LCS analyses, nor do the methods provide acceptability criteria for relative percent differences (RPDs) for the MS/MSD analysis. Refer to the QAPP for project-specific criteria for recoveries and RPDs for these analyses. For the data usability evaluation, the acceptability criteria of these analyses shall be:

   a. The BS and LCS analyses shall display recoveries within 85-115%.

   b. The MS/MSD analyses shall display recoveries within 75-125%.

   c. The MS/MSD analyses shall display an RPD of 20% or less.

3. MS/MSD analyses shall not be performed on field or equipment blanks.

D. Evaluation

1. Verify that an MS/MSD was performed 1 in 20 samples (every 10 per SW-846) and a BS (or LCS) was performed 1 for every batch of ≤ 20 samples. (However, refer to the QAPP for project-specific requirements).

2. Verify that there is consistency between the raw data and the recoveries reported.

3. Verify that the MS/MSD recoveries were within the range of 75% to 125% and the BS (LCS) recoveries were within 85 to 115%.

4. Verify that the RPD for the MS/MSD analysis was less than or equal to 20%.

5. Verify that matrix spikes were not performed on field or equipment blanks.

E. Action

1. Any inconsistencies/errors must be resolved by the laboratory. Data are considered tentative until the laboratory resolves these issues.

2. If the MS/MSD or BS (LCS) was not performed at the required frequency, include a statement to this effect in the quality assurance report.

3. If the MS/MSD was performed on a designated field or equipment blank, note the deficiency in the QA report.

4. If the recoveries are outside criteria, the following apply:

<u>Matrix Spikes/Matrix Spike Duplicates</u>

a. < 75% but ≥ 30% "J" (positives) "U" (negatives).
b. < 30% "J" (positives) "R" (negatives).
c. > 125% but ≤ 150% "J" (positives).

<u>Blank Spikes or Laboratory Control Samples</u>

a. < 85% but ≥ 50% "J" (positives) "UJ" (negatives).
b. < 50% "J" (positives) "R" (negatives).
c. > 115% but ≤ 150% "J" (positives).

In all situations above, the validation report must indicate the direction and severity of the bias.

5. If the MS/MSD analysis displays a RPD greater than 20%, flag the positive results in the samples as estimated ("J"). No qualification is necessary for "not-detected" results.

VII. FIELD DUPLICATES

A. Review Items

Form I and raw data

B. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates, which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

C. Criteria

There are no specific review criteria for field duplicate analyses comparability; however, validation criteria are specified below. Refer to QAPP for project-specific requirements concerning frequency of collection of field duplicates and the precision necessary for the data quality objectives.

D. Evaluation

Samples which are field duplicates should be identified. Check the Chain-of-Custody Records or contact the client for field duplicate information. The reviewer should compare the results reported for each sample and duplicate and calculate the relative percent difference (RPD) for the field duplicate pair.

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met.

1. A control limit of ±20% for aqueous samples (±40% for solid samples) for the RPD shall if both the initial sample and field duplicate sample display results greater than 5× the reporting limit.

2. A control limit of ± the reporting limit (±2× the reporting limit for solid samples) shall be used for all samples if either one or both of the initial and field duplicate sample results were less than 5× the reporting limit.

VIII. SAMPLE RESULT VERIFICATION

A. Review Items

Raw data, analytical results forms, and sample delivery group (SDG) case narrative

B. Objective

The objective is to ensure that the reported quantitative results and reporting limits (RLs) are accurate. Transcription errors are often a problem with general chemistry analyses in which direct instrument printouts are not possible. Therefore, a close scrutiny of the analysis logs and reported results is necessary.

C. Criteria

All positive results must be quantitated correctly and within the calibration range of the instrument. The laboratory must provide all raw data to allow for all positive results to be recalculated and all "not-detected" results to be verified.

D. Evaluation

1. Verify all required data is present. Verify all laboratory calculations are present for all positive sample results and QC samples results.

2. Recalculate 100% of the positive sample results.

3. Verify that all positive results were quantitated within the calibrated range.

E. Action

If there are any discrepancies found, the laboratory may be contacted to obtain additional information that could resolve differences. If a discrepancy remains unresolved, the reviewer may determine that qualification of the data is warranted.

1. Any data that is incorrect and/or missing (i.e., sample calculations) must be resolved/submitted by the laboratory.

2. If a positive result for sulfate in a sample was quantitated from an instrument level greater than the calibration range of the instrument, flag the positive result as estimated ("J") and include a deficiency in the quality assurance report.

IX. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results and the project-specific QAPP, and Field Sampling Plan

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the QAPP, Field Sampling Plan, and communications with the client that concerns the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Prepare a fully documented quality assurance review to the client that provides an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his assessment of the usability of the data within the given context.

X. AUTHORITY

This data validation SOP for the analysis for sulfate has been prepared by Environmental Standards, Inc. for the 3M Corporation Cordova projects. This SOP is not to be used for any other project or by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date: _____

Rock J. Vitale, CPC
Director of Chemistry

STANDARD OPERATING PROCEDURES FOR VALIDATION OF COLORIMETRIC ANALYSES*

(MCAWW METHODS 310.2, 325.1, 325.2, 110.1, 330.5, 410.4, 340.1, 340.3, 425.1, 350.1, 350.2, 351.1, 351.2, 351.3, 352.1, 353.1, 353.2, 353.3, 354.1, 430.1, 430.2, 420.1, 420.2, 420.3, 365.1, 365.2, 365.3, 365.4, 370.1, 375.1, 375.2, AND 376.2, AND SW-846 METHODS 9250, 9251, 7196A, 9065, 9066, 9067, 9035, AND 9036)

I. METHOD SUMMARY

The colorimetric methods examined in this SOP are used to determine the concentration of various wet chemistry parameters in aqueous samples. Generally, in colorimetric methods, the target analytes react with various reagents to produce colored complexes which are measure at specific UV wavelengths. The interferences of each method are presented in Table 1 and Table 2.

II. TECHNICAL HOLDING TIMES

A. Review Items

Chain-of-Custody Records, raw data, digestion or distillation logs (if applicable), and analytical result summaries

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of analysis.

C. Criteria

The analyses are required to be performed within the maximum holding times specified in Table 3 which are based on the dates of sample collection. If the project-specific QAPP requirements differ from those presented in the SOP, then technical requirements for sample holding times will be based on the project-specific QAPP. Most methods require all samples to be cooled (to $4 \pm 2°C$). In addition, many methods require samples to be preserved. Follow the preservative requirements in Table 3.

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* **See Section X for Authority and Application of this SOP.**

D. Evaluation

Technical holding times are established by comparing the sampling dates on the Chain-of-Custody forms with the dates of analysis on the analytical result forms and in the raw data. Examine the samples records to determine if samples were properly preserved.

TABLE 1

Methods for Chemical Analysis of Water and Wastes (EPA-600/4-79-020)

Parameter	Method(s)	Absorbance (nm)	Interferences
Alkalinity	310.2	550	turbidity, color
Chloride	325.1, 325.2	480	none specified
		480	none specified
Color	110.1	438, 540, and 590	turbidity
Chlorine	330.5	515	turbidity, color, oxidizing agents
Chemical Oxygen Demand (COD)	410.4	600	chloride ions
Fluoride	340.1	570	none specified
	340.3	650	aluminum
MBAS	425.1	-	chloride ions
Nitrogen Ammonia	350.1	630-660	calcium, magnesium, turbidity, color
	350.2	425	cyanate, residual chlorine
Nitrogen Kjeldahl, Total	351.1	630	iron, chromium, copper
	351.2	not specified	none specified
	351.3	400-425	high nitrate concentrations
Nitrate	352.1	410	strong oxidizing or reducing agents, dissolved organic matter, residual chlorine, ferrous and ferric iron, quadrivalent manganese, uneven temperature
Nitrate-Nitrite	353.1	540	suspended matter, turbidity, oil and grease, high iron concentrations, copper, and other metals
	353.2	540	suspended matter, oil and grease, high iron concentrations, copper, and other metals
	353.3	529	color, sulfide
Nitrite	354.1	540	strong oxidizing and reducing agents, high alkalinity

TABLE 1 (Cont.)

Parameter	Method(s)	Absorbance (nm)	Interferences
NTA	430.1	620	cations (calcium, magnesium, zinc, copper, iron, and manganese)
	430.2	600 or 625	cations (calcium, magnesium, zinc, copper, iron, and manganese)
Phenolics	420.1	460 or 510	sulfur compounds, oxidizing agents
	420.2	505 or 520	sulfur compounds, oxidizing agents
	420.3	490	sulfur compounds, oxidizing agents, phosphate, aldehydes
Phosphorus	365.1	650-660 or 880	high levels of iron, high arsenate, color, turbidity
	365.2	650 or 880	high levels of iron, arsenate,
	365.3	660 or 880	high levels of iron, arsenate
	365.4	not specified	none specified
Silica	370.1	410, 650, 815	color, turbidity, tannin, phosphate, iron, sulfide, contact with glass
Sulfate	375.1	520	cations (calcium, aluminum, iron)
	375.2	460	pH <2, turbidity
Sulfide	376.2	625	dissolved oxygen, color, turbidity

TABLE 2

Test Methods for Evaluating Solid Waste (SW-846)

Parameter	Method(s)	Absorbance (nm)	Interferences
Chloride	9250, 9251	480	none
Chromium, hexavalent	7196A	540	vanadium, mercury, salts, iron, hexavalent molybdenum
Phenolics	9065	460	sulfur compounds, oxidizing agents
	9066	505 or 520	sulfur compounds, oxidizing agents
	9067	490 or 520	sulfur compounds, oxidizing agents, phosphate, aldehydes
Sulfate	9035	520	cations (calcium, aluminum, iron), turbidity
	9036	460	pH <2, turbidity

TABLE 3

Parameter	Container[1]	Preservative[2]	Holding Time[3]
Alkalinity	P, G	Cool, 4°C	14 Days
Chloride	P, G	None Required	28 Days
Chlorine	P, G	None Required	Analyze Immediately[4]
Chromium(VI)	P, G	Cool, 4°C	24 Hrs.
COD	P, G	Cool, 4°C H_2SO_4 to pH < 2	28 Days
Color	P, G	Cool, 4°C	48 Hrs.
Hardness	P, G	HNO_3 to pH < 2	6 Mos.
Fluoride	P, G	None Required	28 Days
MBAS	P, G	Cool, 4°C	48 Hrs.
NTA	P, G	Cool, 4°C	24 Hrs.
Nitrogen Ammonia	P, G	Cool, 4°C H_2SO_4 to pH < 2	28 Days
Kjeldahl, Total	P, G	Cool, 4°C H_2SO_4 to pH < 2	28 Days
Nitrate plus Nitrite	P, G	Cool, 4°C H_2SO_4 to pH < 2	28 Days
Nitrate	P, G	Cool, 4°C	48 Hrs.
Nitrite	P, G	Cool, 4°C	48 Hrs.
Phenolics	G only	Cool, 4°C H_2SO_4 to pH < 2	28 Days
Phosphorous Ortho-phosphate, Dissolved	P, G	Filter on site Cool, 4°C	48 Hrs.
Phosphorus (Hydrolyzable)	P, G	Cool, 4°C H_2SO_4 to pH < 2	28 Days
Phosphorus (Total)	P, G	Cool, 4°C H_2SO_4 to pH < 2	28 Days

TABLE 3 (Cont.)

Parameter	Container[1]	Preservative[2]	Holding Time[3]
Phosphorus (Total, Dissolved)	P, G	Filter on site Cool, 4°C H_2SO_4 to pH < 2	24 Hrs.
Silica	P only	Cool, 4°C	28 Days
Sulfate	P, G	Cool, 4°C	28 Days
Sulfide	P, G	Cool, 4°C add 2 mL zinc acetate plus NaOH to pH > 9	7 Days

1 Plastic (P) or Glass (G).
2 Sample preservation should be performed immediately upon sample collection.
3 From sample collection to sample analysis.
4 For the data usability evaluation, a 24-hour holding time will be used for chlorine.

E. Action

If technical holding times are exceeded, sample preservation was not performed, or the temperature of the samples was greater than 6°C, document the deficiency in the quality assurance review and qualify the sample results according to the following criteria:

1. If holding times have been exceeded, qualify the positive results as estimated ("J") and qualify the "not-detected" results as "UJ".

2. If holding times have been grossly exceeded (sample analysis exceeds 2× the technical holding time), qualify the positive results as estimated ("J") and the "not-detected" results as unreliable ("R").

3. If an indication of chemical preservation of samples was not provided on the Chain-of-Custody Records, contact the field sampling team or the client for verification of correct sample preservation. If it can be documented that preservation was not performed, or if the pH of the samples upon receipt at the laboratory was not appropriate, flag all positive results as estimated ("J") and all "not-detected" results as "UJ".

4. If the temperature of samples upon receipt at the laboratory exceeds 10°C, attempt to ascertain how the temperature was obtained. If the temperature was obtained from a temperature bottle or an IR gun and the temperature is greater than 10°C, qualify positive results for analytes which require temperature preservation as estimated ("J") and "not-detected" results as "UJ".

III. INITIAL CALIBRATION

A. Review Items

Quality control summary forms and raw data

B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative and qualitative data. An initial calibration curve demonstrates that the instrument is

capable of acceptable performance, with respect to sensitivity and linearity, at the beginning of the analysis and continuing calibration verification documents that the initial calibration is still valid.

C. Criteria

Most of the methods do not give any guidance on the generation of initial calibration curves for the analysis except that a series of standards should be used to prepare a calibration curve. Unless specified in the project-specific QAPP and/or laboratory analytical SOPs, the following will be used to assess the acceptability of the calibration curve:

1. The laboratory shall use a minimum of four-point initial calibration sequence (a blank and three standards) for instrument standardization, unless otherwise specified in the method or laboratory analysis SOP.

2. The correlation coefficient for the linear initial calibration curve shall be ≥ 0.995; if the correlation coefficient is less than 0.995, the laboratory shall prepare new standards, set up the instrument again and recalibrate the instrument.

3. All positive results in the samples shall be reported from instrument levels which are within the calibration range of the instrument. If the instrument level for a sample exceeds the highest initial calibration standard concentration, the sample shall be diluted with reagent water (free of target analytes) and reanalyzed.

D. Evaluation

1. Verify that at least a four-point calibration was performed and that the correlation coefficient for a linear calibration curve is at least 0.995.

2. Verify that all samples have an associated initial calibration. Verify that all samples analyzed for phenolics using SW-846 Methods 9065, 9066, and 9067, and for sulfate using SW-846 Methods 9035 and 9036 have an associated initial calibration which consists of a blank and three standards, for every hour of continuous sample analysis.

3. Recalculate the correlation coefficient.

E. Action

1. If a method requires the preparation of a calibration curve using a specific number of standards and there is an indication that the method (or laboratory SOP) requirements were not followed, document the deficiency in the quality assurance review. Use professional judgment to determine if data should be qualified due to this deficiency.

2. If the correlation coefficient is < 0.995 for linear calibration curve, qualify all positive results as estimated ("J").

3. Any differences/inconsistencies observed in the raw data from what the laboratory has reported must be resolved by the laboratory.

4. If a reported result is based on an instrument level which is greater than the calibration range of the instrument and the laboratory did not dilute and reanalyze the sample, include a statement to this fact in the quality assurance review. In addition, qualify the positive result as estimated ("J").

IV. CONTINUING CALIBRATIONS

A. Review Items

Quality control summary forms and raw data

B. Objective

The purpose of the continuing calibration analysis is to demonstrate acceptable instrument response throughout the period of time during which samples are analyzed. Instrument drift or analytical problems, which may have an adverse effect on the analytical results, is detected by poor results for the continuing calibration analyses.

C. Criteria

EPA Method 375.2 and SW-846 Method 9036 for sulfate analysis require the analysis of a "control" standard every hour to assure that the system remains properly calibrated. EPA Method 365.2 for phosphorous analysis requires the analysis of two standards with each batch of samples, with a recovery limit of ±2%

of the true value. EPA Method 351.3 for nitrogen (Kjeldhahl) requires the analysis of two digested and distilled standards with every batch of samples. The results for these standards must agree with the results of the untreated standard, otherwise corrective action must be taken. All SW-846 Methods (7196A for hexavalent chromium; 9250 and 9251 for chloride; 9065, 9066, and 9067 for phenolics; and 9035 and 9036 for sulfate) require the analysis of a "check" standard every 15 samples analyzed. However, most of the methods do not specify criteria for the frequency of continuing calibration analyses and the acceptable recoveries in the continuing calibration standards. Refer to the QAPP and laboratory analysis SOPs for project-specific requirements for continuing calibrations. For the purposes of data validation, the following criteria shall be used for assessing data quality:

1. The continuing calibration standard shall be analyzed at the beginning and end of the sample analysis, and after every 15 sample analyses.

2. The continuing calibration standard shall display recoveries within the range of 85-115%. Otherwise, restandardize the instrument, reverify the standardization (with the continuing calibration standard), and reanalyze all samples analyzed since the last compliant continuing calibration.

D. Evaluation

1. Review the raw data recordings and/or notebook pages to verify consistency between dates and times and consistency between raw data and QA summary forms.

2. Verify that continuing calibration standards were performed at a minimum of once after every 15 samples, before all samples are analyzed, and after the last sample is analyzed.

3. Verify that the percent recoveries were within 85-115% of the values obtained in the initial calibration.

E. Action

1. Any inconsistencies/errors must be resolved by the laboratory. Analytical results should be considered tentative until the laboratory resolves these issues.

2. For continuing calibration outside the 85-115% criteria, positive results should be considered estimated and flagged "J". If the recovery exceeds 130% or is less than 70%, flag all positive result as unusable ("R").

   Note: The continuing calibration standard should be applied to samples on both "sides" (before and after) until a compliant standard is obtained in both directions.

3. If a continuing calibration analysis displays a recovery less than 85%, qualify the "not-detected" results as estimated ("UJ"). If the analysis displays recoveries less than 70%, flag "not-detected" results as unusable ("R"). "Not-detected" results are not qualified if high recoveries are reported for the continuing calibration analyses.

4. If continuing calibration standards were not performed at the method (or laboratory analysis SOP) required frequency, note the deficiency in the quality assurance review.

5. If a recovery outside the method or laboratory acceptance window is reported for a continuing calibration and the laboratory did not restandardize the instrument and reanalyze the associated samples, include a statement to this fact in the quality assurance review.

V. BLANKS

A. Review Items

Analytical results forms, quality control summary forms, and raw data

B. Objective

Method blanks are reagent water blanks (initiated by the laboratory) carried through the sample preparation and analysis steps. Therefore, they monitor sample contamination which may occur during these steps in the laboratory. Calibration blanks are reagent water that has not undergone any sample preparation steps. They monitor instrument drift which may result in false positive or false negative results for the samples. Field and/or equipment blanks monitor the possible contamination of samples in the field (during the sampling event), during the shipment of the samples, and during the preparation and analysis of the samples.

C. Criteria

All SW-846 Methods, EPA Method 370.1 for silica analysis, and EPA Method 365.2 for phosphorus require the analysis of one method blank with every batch of samples. Several methods require the analysis of calibration blanks. However, most methods do not give any guidance to the frequency of analysis or acceptable results for method blanks or calibration blanks. Refer to the QAPP for project-specific requirements for these quality control analyses, and for the frequency of collection of field and/or equipment blanks and the acceptable results for these field quality control blanks. For data validation purposes, the following criteria shall be used to assess the quality of the reported analytical results:

1. A method blank shall be prepared with every batch of samples prepared for analysis or for every 20 samples, whichever is more frequent.

2. The method blank and the continuing calibration blanks shall not display positive results greater than the reporting limit for the analysis.

3. The continuing calibration blank shall be analyzed immediately after every continuing calibration standard.

4. The field, equipment, and/or rinse blanks shall not display results greater than the reporting limit.

5. The laboratory shall not perform blank-subtraction when reporting results in the samples.

D. Evaluation

1. Verify the reported results against the raw data recordings and/or notebook pages to determine consistency and if these blanks have acceptable calibrations.

2. Verify that every sample within the data set has an associated method blank and calibration blanks.

3. Verify that each method blank and calibration blank does not contain target analytes in excess of the reporting limit.

4. Verify there is a field and/or equipment blank for every data set of 20 samples or less (or per the requirement in the QAPP).

5. Verify that the field and/or equipment blanks do not contain target analytes above the reporting limit.

E. Action

1. Any missing items, inconsistencies, or errors must be resolved by the laboratory. Until the laboratory clarifies/resubmits these items, the associated results are designated as tentative.

2. If the laboratory has utilized blank subtraction, the laboratory must resubmit the data unsubtracted.

3. If a field and/or equipment blank is not present, note this in the quality assurance review.

4. If the laboratory did not prepare and analyze a method blank, or analyze the continuing calibration blanks at the proper frequency, include a statement to this fact in the quality assurance review.

5. The results of all laboratory blanks should be applied to all samples.

6. The results of the field blank should be applied to all samples collected on the same day.

7. In instances where more than one blank is associated with a given sample, qualification will be based upon a comparison with the associated blank having the highest concentration of a contaminant.

8. If any target analyte is present in any blank above the instrument detection limit, the following apply:

   a. If a sample result is less than five times the concentration of the target analyte in the blank, the sample result should be considered "not-detected" and qualified "U".

   b. If the sample result is greater than five times the blank result, no action will be taken.

c. If an analyte is detected in the blank but not in the samples, no action will be taken.

VI. MATRIX SPIKES/MATRIX SPIKE DUPLICATES AND BLANK SPIKES OR LABORATORY CONTROL SAMPLES

A. Review Items

Analytical result forms, quality control summary forms, and raw data

B. Objective

Data for matrix spikes (MS)/matrix spike duplicates (MSDs) are generated to determine long-term accuracy and precision of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. The data for blank spikes (BSs) or laboratory control samples (LCSs) are generated to determine analytical accuracy. The results of blank spikes (or LCSs) are used to assess accuracy of the entire sample batch.

C. Criteria

The SW-846 methods require the analysis of a matrix spike sample for every 10 samples, but they do not specify criteria for acceptable recovery range for matrix spike or for BS (LCS) analysis. The EPA methods do not specify criteria for the frequency of MS/MSD, BS, or LCS analysis or the acceptable recovery range. Refer to the QAPP and laboratory analytical SOPs for project-specific requirements concerning these quality control analyses. For data validation purposes, the following criteria shall be used to assess data quality:

1. An MS/MSD pair shall be prepared with every batch of samples prepared for analysis or for every 20 samples, whichever is more frequent.

2. The laboratory's recovery QC limits will be used unless they are overly expanded, in which case, the acceptable recovery range for the MS/MSD pair will be 75-125%. Spike recovery limits do not apply when the sample concentration exceeds the spike concentration by more than a factor of four.

3. The laboratory's RPD QC limits will be used unless they are overly expanded, in which case, the maximum relative percent difference between the results in the MS/MSD analysis will be 20%.

4. The BS sample (or LCS) shall be prepared with every batch of samples prepared for analyses or for every 20 samples, whichever is more frequent.

5. The acceptable recovery range for the LCS and BS analyses will be the laboratory's QC limits, unless they are overly expanded, in which case the acceptable recovery range will be 80-120%. If an unacceptable recovery is obtained for the BS or LCS analysis, all associated samples shall be reprepared and reanalyzed.

6. The MS/MSD analysis will not be performed on a known field and/or equipment blank.

D. Evaluation

1. Verify that the MS/MSD and LCS or BS samples were prepared and analyzed at the proper frequency.

2. Verify that there is consistency between the raw data and the recoveries reported.

3. Verify that the MS/MSD recoveries are within the laboratory's limits or within the range of 75-125%.

4 Verify that the BS and the LCS recoveries were within the laboratory's limits or within the range of 80-120%.

5. Verify that MS/MSD analysis was not performed on a designated field and/or equipment blank.

6. Verify that if the BS or LCS analysis displayed an unacceptable recovery, the laboratory reprepared and reanalyzed all associated samples.

E. Action

1. Any inconsistencies/errors must be resolved by the laboratory. Data are considered tentative until the laboratory resolves these issues.

2. If the MS/MSD was performed on a designated field and/or equipment blank, note the deficiency in the quality assurance report.

3. If the recoveries for the MS/MSD are outside criteria, the following apply:

   a. If %R < 75% but > 30% , qualify positive results as estimated "J" and "not-detected" results "UJ".

   b. If %R < 30% qualify positive results as estimated "J" and "not-detected" results as unreliable ("R").

   c. If %R > 125%, qualify positive results as estimated "J". The "not-detected results do not require qualification.

4. If the recoveries for the BS or LCS are outside criteria, the following apply:

   a. If %R < 80% but > 50%, qualify positive results as estimated ("J") and "not-detected" results "UJ".

   b. If %R < 50%, qualify positive results as estimated ("J") and "not-detected" results as unreliable ("R").

   c. If %R > 120% qualify positive results as estimated ("J"). The "not-detected" results do not require qualification.

5. If the relative percent difference for the results from the MS/MSD analysis exceeds the laboratory's limits or 20%, flag all positive results in the associates samples as estimated ("J"). Qualification of "not-detected" results in the samples is not necessary.

6. If the BS or LCS analysis displays an unacceptable recovery, and the laboratory did not reprepare and reanalyze the samples, note the deficiency in the quality assurance review.

VII. FIELD DUPLICATES

A. Review Items

Form I and raw data

B. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates, which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

C. Criteria

There are no specific review criteria for field duplicate analyses comparability; however, validation criteria are specified below. Refer to QAPP for project-specific requirements concerning frequency of collection of field duplicates and the precision necessary for the data quality objectives.

D. Evaluation

Samples which are field duplicates should be identified. Check the Chain-of-Custody Records or contact the client for field duplicate information. The reviewer should compare the results reported for each sample and duplicate and calculate the relative percent difference (RPD) for the field duplicate pair.

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met.

1. A control limit of $\pm 20\%$ for aqueous samples ($\pm 40\%$ for solid samples) for the RPD shall if both the initial sample and field duplicate sample display results greater than $5\times$ the reporting limit.

2. A control limit of ± the reporting limit (±2× the reporting limit for solid samples) shall be used for all samples if either one or both of the initial and field duplicate sample results were less than 5× the reporting limit.

VIII. SAMPLE RESULT VERIFICATION

A. Review Items

Analytical results forms and raw data

B. Objective

The objective is to ensure that reported quantitative results and reporting limits (RLs) are accurate and that all reported positive results were calculated within the calibration range of the instrument.

C. Criteria

All positive results must be quantitated correctly and within the calibration range of the instrument. The laboratory shall provide all raw data necessary to recalculate all positive results and to verify the reported "not-detected" results from the raw data.

D. Evaluation

1. Verify that all required data is present. Verify that all laboratory calculations are present for all positive sample results and QC sample results.

2. Recalculate and confirm the positive sample results.

3. Verify that all positive results were quantitated within the calibrated range.

E. Action

If there are any discrepancies found, the laboratory may be contacted to obtain additional information that could resolve differences. If a discrepancy remains unresolved, the reviewer may determine that qualification of the data is warranted.

1. Any data that is incorrect and/or missing (i.e., sample calculations) must be resolved/submitted by the laboratory.

2. Reported positive results quantitated beyond the calibrated range should be considered estimated and flagged "J".

IX. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results, the QAPP and Field Sampling Plan

B. Objective

The overall assessment of a data package is a quality assurance review in which the data reviewer expresses concerns and comments on the quality and the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the QAPP and Field Sampling Plan, and communicate with the client any concerns relating to the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Write a fully documented quality assurance review which provides the client with an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his assessment of the usability of the data within the given context.

X. AUTHORITY

This data validation SOP for colorimetric analyses has been prepared by Environmental Standards, Inc. for use on the 3M Corporation Cordova projects. This SOP is not to be used for any other project or by another entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date: _____

Rock J. Vitale, CPC
Director of Chemistry

APPENDIX 11

INTERNAL FIELD AUDIT CHECKLIST

RUST **Rust Environment & Infrastructure Inc.**

3M CORDOVA
INTERNAL FIELD AUDIT CHECKLIST

Event (Dates): _____
Field Personnel: _____

Audit Completed By: _____

Work Performed _____
_____
_____
_____

Work Orders Obtained? Yes ___ No ___ Comments _____

Calibrations (Should be entered in Field Log Book and on appropriate forms)
Yes ___ No ___ Comments _____

Field Measurements (Should be entered in Field Log Book, Lab Templates, and appropriate forms)
-Water Levels (Initial)? Yes ___ No ___ Comments _____
-Water Levels (Final)? Yes ___ No ___ Comments _____
-pH? Yes ___ No ___ Comments _____
-Conductivity? Yes ___ No ___ Comments _____
-Temperature? Yes ___ No ___ Comments _____
-Turbidity? Yes ___ No ___ Comments _____

Lab Template Data Complete? Yes ___ No ___ Comments _____

QC Samples Collected
-Blind Dups ___ Equip Blank ___ Field Blank ___ Trip Blank ___ MS/MSD ___

Chain-of-Custodies Complete? Yes ___ No ___ Comments _____

Custody Seal Numbers Recorded? Yes ___ No ___ Comments _____

Sample Shipment Documentation Complete? Yes ___ No ___ Comments _____

Field Log Book Complete? Yes ___ No ___ Comments _____

Any Field Delays? _____

Problems/Corrective Action? _____

Remaining Action Items? _____

APPENDIX 12

ENVIRONMENTAL STANDARDS
FIELD AUDIT CHECKLIST

3M

CORDOVA, ILLINOIS

FIELD AUDIT CHECKLIST

RCRA FACILITY INVESTIGATION

FIELD SAMPLING PROGRAM

Project Location: Cordova, Illinois

Environmental Standards' Job #: _____

Date(s) of Field Audit: _____

Time(s) of Field Audit: _____

Environmental Standards' Auditor(s): _____

Rust's Field Sampling Crew: _____

Audit Conducted on the Following:

_____ Pre-Task Planning	_____ Groundwater Sampling
_____ Field Documentation/Records	_____ Decontamination
_____ Sampling Containers	_____ Chain-of-Custody
_____ Field QC Samples	_____ Sample Packaging
_____ Soil Sampling	_____ Waste Management
_____ Field Measurements	_____ Health & Safety

	Y	N	N/A
Pre-Task Planning:			
- Personnel and responsibilities noted	_____	_____	_____
- 3M project-specific SOPs present and in use	_____	_____	_____
- Sampling location (on-site specific map)	_____	_____	_____
- Location number (soil boring, etc.)	_____	_____	_____
- Weather conditions	_____	_____	_____
- Parameters to be sampled identified	_____	_____	_____
- Additional pre-sampling observation (if applicable)	_____	_____	_____

3M (Cont.)

CORDOVA, ILLINOIS

FIELD AUDIT CHECKLIST

RCRA FACILITY INVESTIGATION

FIELD SAMPLING PROGRAM

	Y	N	N/A
Field Documentation/Records:			
- Notebooks - bound-page, numbered, no missing pages	____	____	____
- Appropriate 3M field sampling records in use	____	____	____

	Y	N	N/A
Sample Containers:			
- Proper type and size	____	____	____
- Proper preservation	____	____	____
- Proper labeling	____	____	____
- Proper quantity	____	____	____
- Proper source of container	____	____	____
- Cooler	____	____	____
- Proper ice	____	____	____
- Proper packing material	____	____	____
- Proper custody seals	____	____	____
- Proper courier	____	____	____

3M (Cont.)

CORDOVA, ILLINOIS

FIELD AUDIT CHECKLIST

RCRA FACILITY INVESTIGATION

FIELD SAMPLING PROGRAM

	Y	N	N/A
Field QC Samples:			
- Proper frequency	____	____	____
- Proper field blank(s)	____	____	____
- Proper equipment blank(s)	____	____	____
- Proper trip blank(s)	____	____	____
- Proper duplicate sample(s)	____	____	____
- Proper matrix spike/matrix spike duplicate sample(s)	____	____	____
- Proper water source for blanks	____	____	____

	Y	N	N/A
Soil Sampling:			
- Locations agree with Work Plan	____	____	____
- Locations documented sufficiently	____	____	____
- Sampling times, identifications, and descriptions noted	____	____	____
- Volatiles collected first	____	____	____
- Sample bottles inspected	____	____	____
- Bottles labeled properly	____	____	____
- Proper containers/preservatives	____	____	____
- Proper sample volumes procured	____	____	____
- Proper ice or refrigeration after collection	____	____	____

CORDOVA, ILLINOIS

FIELD AUDIT CHECKLIST

RCRA FACILITY INVESTIGATION

FIELD SAMPLING PROGRAM

	Y	N	N/A
Soil Sampling (Continued):			
- Potential for cross-contamination exists	____	____	____
- Consistency of technique	____	____	____
- Samples collected at proper depths	____	____	____
- Samples screened with HNU	____	____	____
- Description of material logged	____	____	____
- Soils homogenized except for VOAs	____	____	____

	Y	N	N/A
Field Measurements:			
- Proper calibration of pH meter	____	____	____
- Conductivity meter	____	____	____
- Thermometer	____	____	____
- Proper standards of pH meter	____	____	____
- Conductivity meter	____	____	____
- Thermometer	____	____	____

CORDOVA, ILLINOIS

FIELD AUDIT CHECKLIST

RCRA FACILITY INVESTIGATION

FIELD SAMPLING PROGRAM

	Y	N	N/A
Field Measurements (Cont.)			
- Proper units for pH	____	____	____
- Conductivity meter	____	____	____
- Thermometer	____	____	____
- Proper frequency of pH	____	____	____
- Conductivity meter	____	____	____
- Thermometer	____	____	____
- Steady state achieved for pH	____	____	____
- Conductivity	____	____	____
- Temperature	____	____	____
- Proper times/dates purged for pH	____	____	____
- Conductivity	____	____	____
- Thermometer	____	____	____
- Submersible pump positioned properly	____	____	____
- Proper instrument for measuring indicator parameters	____	____	____
- Proper instrument for measuring headspace	____	____	____

3M (Cont.)

CORDOVA, ILLINOIS

FIELD AUDIT CHECKLIST

RCRA FACILITY INVESTIGATION

FIELD SAMPLING PROGRAM

	Y	N	N/A
Groundwater Sampling			
- Water volumes calculated properly	____	____	____
- Monitoring headspace in well	____	____	____
- Interface probe for LNAPL/DNAPL	____	____	____
- Pump properly positioned	____	____	____
- Correct purge rate	____	____	____
- Drawdown less than 3 feet	____	____	____
- Appropriate disposal of purge water	____	____	____
- Bailer and bail line dedicated to each well	____	____	____

	Y	N	N/A
Chain-of-Custody:			
- Client and location	____	____	____
- Sample identification numbers	____	____	____
- Date collected	____	____	____
- Time collected	____	____	____
- Matrix	____	____	____
- Number of containers	____	____	____
- Preservation technique	____	____	____

3M (Cont.)

CORDOVA, ILLINOIS

FIELD AUDIT CHECKLIST

RCRA FACILITY INVESTIGATION

FIELD SAMPLING PROGRAM

	Y	N	N/A
Chain-of-Custody (Continued):			
- Blanks labeled	____	____	____
- Proper transfer signatures	____	____	____
- Proper transfer time and date	____	____	____
- Proper continuity	____	____	____
- Sample travel time reasonable	____	____	____
- Airbill and courier name	____	____	____

	Y	N	N/A
Decontamination:			
- Proper frequency	____	____	____
- Proper method(s) considering organic analytes	____	____	____
- Proper method(s) considering inorganic analytes	____	____	____
- Each device cleaned			
List 1)	____	____	____
List 2)	____	____	____
List 3)	____	____	____
List 4)	____	____	____
List 5)	____	____	____

CORDOVA, ILLINOIS

FIELD AUDIT CHECKLIST

RCRA FACILITY INVESTIGATION

FIELD SAMPLING PROGRAM

	Y	N	N/A
Decontamination (Continued):			
- Disposable equipment collected and removed for disposal	____	____	____
- Proper decontamination area used	____	____	____
- Dedicated equipment	____	____	____
- Clean plastic sheeting	____	____	____

	Y	N	N/A
Sample Packaging:			
- Samples packed to avoid breakage	____	____	____
- Sufficient ice packs	____	____	____
- Absorbent material sufficient	____	____	____
- Chain-of-Custody in Ziplock® in cooler	____	____	____
- Custody seals initialed and present	____	____	____
- Strapping tape adequate	____	____	____
- Cooler labels adequate	____	____	____

3M (Cont.)

CORDOVA, ILLINOIS

FIELD AUDIT CHECKLIST

RCRA FACILITY INVESTIGATION

FIELD SAMPLING PROGRAM

	Y	N	N/A
Waste Management:			
- 3M waste source codes	____	____	____
- Proper segregation	____	____	____
- Proper container labels	____	____	____

	Y	N	N/A
Health & Safety:			
- Proper level of protective clothing	____	____	____
- HASP plan on-site with emergency contacts	____	____	____
- Monitoring equipment present	____	____	____
- First aid kit in field office	____	____	____
- Contaminated PPE disposed of properly	____	____	____

	Y	N	N/A
General:			
- Personnel conducting investigation professionally	____	____	____
- Project objectives understood by personnel	____	____	____
- Records taken in a clean and legible manner	____	____	____
- Field crew organized	____	____	____

3M (Cont.)

CORDOVA, ILLINOIS

FIELD AUDIT CHECKLIST

RCRA FACILITY INVESTIGATION

FIELD SAMPLING PROGRAM

	Y	N	N/A
General (Continued):			
- Continuity in the process	____	____	____
- Weather conditions affecting sample quality	____	____	____
- Field office organized	____	____	____

Audit Summary and Comments:

_____

_____

_____

_____

_____

_____

_____

_____

_____

_____

Signed by: _____ Print: _____

Date: _____

APPENDIX 13

INTERNAL LABORATORY AUDIT CHECKLIST

QUANTERRA ENVIRONMENTAL SERVICES

1996 QUALITY SYSTEMS AUDIT CHECKLIST

QUALITY/OPERATION FILES

On-Site Audit Date: _____

_____ **LABORATORY**

QUANTERRA 1996 QUALITY SYSTEMS AUDIT CHECKLIST

Location:_____ Date:_____ Auditor:_____

Personnel Contacted:_____

I. QUALITY/OPERATIONS FILES

	Yes	No	N/A	
A. Quality Assurance Documents				
1. Are Quality/Operations (Q/O) records indexed, current, labeled, and secure?				
Additional item: *[QA Documents]*				
2. Quality Assurance Management Plan (QAMP) Appendix Latest Revision: _____ Date: _____				
a. Is the QAMP Appendix current, complete, and accurate through the use of either document change forms or revision? (Revised every 6 months)				
b. Are previous revisions available in the Quality/Operations records? Rev. 0, Date: _____ Rev. 1, Date: _____				
Additional item: *[QA Documents]*				
3. **Thermometers/Weights/Balances/Pipettes - Quality Records** *[QAMP, Table 8.5-8, Periodic Calibrations]*				
a. Does documentation exist for certification of a NIST-traceable thermometer(s) within the last three years?				
b. Does documentation exist for annual calibration of all working thermometers against a NIST-traceable thermometer?				
c. Does documentation exist for external certification of all				

Location:_____ Date:_____ Auditor:_____

Personnel Contacted:_____

I. QUALITY/OPERATIONS FILES (continued)

	Yes	No	N/A	
class S weights within the last three years?				
d. If class S-traceable weights are used, are they calibrated against class S weights at least once per month? Does documentation exist?				
e. Are balances serviced and calibrated by an external agency at least annually? Does documentation exist?				
f. Does documentation of quarterly balance calibrations exist for all working balances?				
g. Does documentation of calibration exist for all working pipettes?				
Additional item: *[Equipment/Facility Records]*				
4. **Controlled Distributions**				
a. Does the QA Manager or designee (name) control the distribution of:				
QAMP with Appendix (locally)? QMP?				
SOPs?				
QAPjPs? (as appropriate)				
Software?				
b. Are revisions to these documents reviewed, approved, and controlled in the same manner as the originals?				
Additional item: *[Controlled Distributions]*				

Location:_____ Date:_____ Auditor:_____

Personnel Contacted:_____

I. QUALITY/OPERATIONS FILES (continued)

	Yes	No	N/A	
B. Audit/Spot Assessment Records *(REF: Section 9.2.4, QMP, Rev. 0, Aug 1, 1994)*				
1. Internal Spot Assessments:				
a. Performed a minimum of monthly?				
b. Reports available?				
c. Nonconformances resolved in a timely manner?				
d. Corrective actions verified? (follow-up performed?)				
2. Internal Quality Systems Audits *(REF: Section 9.2.2, QMP, Rev.0, Aug 1, 1994)*				
a. Performed at required frequency?				
b. Reports available?				
c. Findings and observations resolved in a timely manner?				
d. Corrective actions verified?				
e. Responses submitted by the auditor's due date?				
3. External Audits (Take one file at random and review. This is a spot check only.)				
a. Is the report available?				
b. Is the response submitted in a timely manner or by the auditor's due date?				
c. Findings and observations resolved in a timely manner?				
d. Corrective actions verified?				
Additional item: *[Audit/Spot Assessment Records]*				

Location:_____ Date:_____ Auditor:_____

Personnel Contacted:_____

I. QUALITY/OPERATIONS FILES (continued)

	Yes	No	N/A	
C. Subcontractor Records *(REF: Section 4.3, QMP, Rev.0, Aug 1, 1994)*				
1. Has the use of the subcontractor(s) been approved at a corporate level?				
2. Has a QA systems audit been performed?				
3. Is an audit report available?				
4. Have corrective actions been verified?				
5. Has the laboratory been evaluated at least annually?				
6. List all subcontractors used and the most recent audit date: 1. _____ Audit Date: _____ 2. _____ Audit Date: _____				
Additional item: *[Subcontractor Records]*				
D. Performance Evaluation Sample Records *(REF: QAMP, Section 8.4.4)*				
1. Reports available (both internal and external)?				
2. "Not Acceptable" parameters investigated, resolved, and documented?				
3. Corrective actions verified and documented?				
Additional item: *[PE Sample Records]*				

Location:_____ Date:_____ Auditor:_____

Personnel Contacted:_____

I. QUALITY/OPERATIONS FILES (continued)

	Yes	No	N/A	
E. Nonconformance/Corrective Action *(REF: Section 9.1, QMP, Rev.0, Aug 1, 1994)*				
1. Is the log complete?				
2. Are Nonconformance Memos routed appropriately and in a timely manner?				
3. Are signed/dated originals placed in the project file when appropriate?				
4. Are corrective actions verified and logged in a timely manner?				
5. Are all required signatures present?				
Additional item: *[Nonconformance/Corrective Action]*				
F. Computer Software Verification/Validation Records *(REF: Section 6.0, QMP, Rev.0, Aug 1, 1994)*				
1. Are all computer programs used for manipulation of data completely documented (validated) and verified?				
2. Are spreadsheet program applications verified annually with a standard data set?				
3. Is computer input properly checked? (100% for transcription errors)				
4. Is computer output properly identified with program name,				

Location:_____ Date:_____ Auditor:_____

Personnel Contacted:_____

I. QUALITY/OPERATIONS FILES (continued)

	Yes	No	N/A	
project number, date, time, and operator?				
Additional item: *[Software]*				
G. Training Files (See Supplement G) *(REF: Section 3.0, QMP, Rev.0, Aug 1, 1994)*				
1. Do personnel have qualifications documented?				
2. Does a formal, documented training program exist consisting of:				
Technical training for new analysts?				
Annual evaluation of training file by an appropriate supervisor?				
Quality assurance orientation/training for all staff members?				
3. Based on the review of training files, are individual training files current and complete?				
Additional item: *[Training Files]*				

Location:_____ Date:_____ Auditor:_____

Personnel Contacted:_____

I. QUALITY/OPERATIONS FILES (continued)

SUPPLEMENT G.: **Individual training files review:**	Name:	Name:
Title (organization chart):		
Title (resume):		
Degree/Year/Discipline? Certificates/Diplomas?		
Resume/Current?		
Job Description?		
Listing of qualified procedures? procedures? procedures?		
PE/qualification samples? On-the-Job Training?		
QA Orientation?		
QA Exam?		
LST Training?		
CHP Training?		

Location:_____ Date:_____ Auditor:_____

Personnel Contacted:_____

I. QUALITY/OPERATIONS FILES (continued)

APPENDIX 14

SUMMARIES OF PREVIOUS DETECTIONS IN GROUNDWATER, SOIL, AND SLUDGE AT THE 3M CORDOVA, ILLINOIS SITE

TABLE A14-1. SUMMARY OF PREVIOUS DETECTIONS IN GROUNDWATER, SOIL AND SLUDGE AT THE 3M CORDOVA, ILLINOIS SITE NOT RFI-RELATED DATA

COMPOUND	CONCENTRATION RANGE	CONCENTRATION UNITS	REFERENCE	REVISED DECEMBER 1995 REGION 5 DQL/MCL	DQL/MCL UNITS
Sludge Data					
Acetone	ND-150,000	µg/kg	I	2,000,000	µg/kg
Acetonitrile	ND-240,000	µg/kg	I	390,000	µg/kg
Aluminum	345-11,000	mg/kg	D1		
	66.5-140	mg/L	D1		
Ammonia	ND- 1,300	mg/L	D1		
	ND-1,685	mg/kg	D1		
Anthracene	0.5	mg/kgd	F	1.9	mg/kg
Antimony	31-160	mg/kg	I	31	mg/kg
	0.038	mg/L	F	0.015	mg/L
Arsenic	2.2-4.2	mg/kg	I	0.32	mg/kg
	2	mg/kg	D1	0.32	mg/kg
	0.07	mg/L	D1	0.000038	mg/L
Barium	67-165	mg/kg	I	5,300	mg/kg
Bis (2-Ethylhexyl) Phthalate	0.2	mg/kgd	F	32	mg/kg
Boron	0.5	mg/kg	D1		
Cadmium	ND-0.87	mg/L	D1	0.018	mg/L
	ND-40	mg/kg	I	38	mg/kg
	ND-2	mg/kg	D1	38	mg/kg
Calcium	2,340-30,060	mg/kg	D1		
Chromium	29-40	mg/kg	I	210	mg/kg
	ND-85	mg/kg	D1	210	mg/kg
	0.22	mg/L	F	0.18	mg/L
	0.32-4	mg/L	D1	0.18	mg/L
	46	mg/kgd	F	210	mg/kg
Chrysene	0.5	mg/kgd	F	24	mg/kg
Cobalt	30-76	mg/kg	I	NA	mg/kg
	ND-6,400	mg/kg	D1	NA	mg/kg
	0.2-56	mg/L	D1	NA	mg/L
Copper	0.22	mg/L	F	1.4	mg/L
	38-130	mg/kg	I	2,800	mg/kg
	0.6-12	mg/L	D1	1.4	mg/L
	ND-110	mg/kg	D1	2,800	mg/kg
	30	mg/kgd	F	2,800	mg/kg
Cyanide	0.95	mg/L	F	0.0062	mg/L
	0.2	mg/L	D1	0.0062	mg/L
delta-BHC	1.1	µg/kgd	F	NA	µg/kg
Dichloromethane	ND-19,000	µg/kg	I	11,000	µg/kg
Ethylbenzene	27,000-140,000	µg/kg	I	2,900,000	µg/kg
Fluoranthene	0.9	mg/kgd	F	2,600	mg/kg
Fluorene	4.2	mg/kgd	F	300	mg/kg
Heptachlor	2.3	µg/kgd	F	99	µg/kg
Iron	46-86,000	mg/L	D1	0.3*	mg/L
	76-550,000	mg/kg	D1		
Kjeldahl Nitrogen	320-2,900	mg/kg	D1		
	ND-2,500	mg/L	D1		

TABLE A14-1. SUMMARY OF PREVIOUS DETECTIONS IN GROUNDWATER, SOIL AND SLUDGE AT THE 3M CORDOVA, ILLINOIS SITE NOT RFI-RELATED DATA

COMPOUND	CONCENTRATION RANGE	CONCENTRATION UNITS	REFERENCE	REVISED DECEMBER 1995 REGION 5 DQL/MCL	DQL/MCL UNITS
Lead	ND-20	mg/L	D1	0.004	mg/L
	4.4-15	mg/kg	I	400	mg/kg
	ND-80	mg/kg	D1	400	mg/kg
	24	mg/kgd	F	400	mg/kg
	0.15	mg/L	F	0.004	mg/L
Lithium	0.08	mg/L	D1		
Magnesium	177-3,000	mg/kg	D1		
	57.5-123	mg/L	D1		
Manganese	0.4-680	mg/L	D1		
	2.9-6,900	mg/kg	D1		
Mercury	0.0028-0.58	mg/kg	D1	23	mg/kg
	ND-1.3	mg/kg	I	23	mg/kg
	0.009	mg/L	F	0.011	mg/L
	0.24	mg/kgd	F	23	mg/kg
	0.022-0.14	mg/L	D1	0.011	mg/L
Naphthalene	0.5	mg/kgd	F	800	mg/kg
Nickel	76-140	mg/kg	I	1,500	mg/kg
	0.38	mg/L	F	0.73	mg/L
	210	mg/kgd	F	1,500	mg/kg
	0.98-600	mg/kg	D1	1,500	mg/kg
	ND-220	mg/L	D1	0.73	mg/L
Nitrate-N	ND-280	mg/L	D1	10*	mg/L
	0.76-510	mg/kg	D1		
Nitrite-N	0.12	mg/L	D1	1*	mg/L
PCB-Aroclor 1242	1,400-4,400	µg/kg	I	66	µg/kg
PCB-Aroclor 1254	2.0	µg/L	F	0.0087	µg/L
PCB-Aroclor 1260	ND-1,700	µg/kg	I	66	µg/kg
Phenanthrene	8.0	mg/kgd	F	NA	mg/kg
Potassium	193	mg/L	D1		
Propionitrile	ND-210,000	µg/kg	I	NA	µg/kg
Pyrene	0.3	mg/kgd	F	2,000	mg/kg
Silver	0.042	mg/L	F	0.18	mg/L
	1.0	mg/kgd	F	380	mg/kg
Sodium	1,750-2,200	mg/L	D1		
	1,183-20,000	mg/kg	D1		
TCLP Barium	0.1 - 0.18	mg/L	P	NA	
TCLP Methyl Ethyl Ketone	0.050	mg/L	P	NA	
Thallium	ND-2.2	mg/kg	I	6,100	µg/kg
Titanium	392	mg/kg	D1		
Toluene	6.0	mg/kg	F	1,900	mg/kg
	330	µg/L	F	720	µg/L
	ND-1.0	µg/L	K	720	µg/L
	160-670	mg/kg	I	1,900	mg/kg
Total Fluoride	80-160	mg/L	D1		
	250-33,700	mg/kg	D1		

TABLE A14-1. SUMMARY OF PREVIOUS DETECTIONS IN GROUNDWATER, SOIL AND SLUDGE AT THE 3M CORDOVA, ILLINOIS SITE NOT RFI-RELATED DATA

COMPOUND	CONCENTRATION RANGE	CONCENTRATION UNITS	REFERENCE	REVISED DECEMBER 1995 REGION 5 DQL/MCL	DQL/MCL UNITS
Total Phenols	0.85	mg/kgd	F	39,000 (5)	mg/kg
	ND-135	µg/L	K		
Total Phosphorous	24-1,559	mg/L	D1		
	64-36,000	mg/kg	D1		
Vanadium	ND-11	mg/kg	I	540	mg/kg
Xylene	110,000-650,000	µg/kg	I	980,000	µg/kg
Zinc	30-78	mg/kg	I	23,000	mg/kg
	0.37	mg/L	F	11	mg/L
	73	mg/kgd	F	23,000	mg/kg
	1-640	mg/kg	D1	23,000	mg/kg
	0.7-64	mg/L	D1	11	mg/L
Groundwater Data					
Alk M	37 - 100	mg/L	D2		
Alk P	0 - 100	mg/L	D2		
Aluminum	ND - 140	mg/L	D2		
Ammonia	ND - 160	mg/L	D2		
Ammonia as N	ND - 190	mg/L	D2		
Benzene	ND-0.04	mg/L	H	0.00039	mg/L
Cadmium	ND - 0.02	mg/L	D2	0.018	mg/L
Chlorine	1 - 20	mg/L	D2		
Chloroform	ND-5	µg/L	F	0.16	µg/L
Di-n-Butyl Phthalate	ND-16	µg/L	F	3,700	µg/L
Flourine	0.2 - 0.3	mg/L	D2	0.31	mg/L
Kjeldahl Nitrogen	ND - 14.6	mg/L	D2		
Mercury	ND -0.7	mg/L	D2	0.011	mg/L
Nitrate	ND - 140	mg/L	D2	10*	mg/L
Nitrate as N	ND - 160	mg/L	D2		
Nitrite as N	ND - 8.25	mg/L	D2		
Nitrite plus Nitrate as N	ND - 110	mg/L	D2		
Nitrogen	ND - 0.02	mg/L	D2		
pH	4.37-8	units	H		
Selenium	ND-0.004	mg/L	F	0.18	mg/L
Sodium	2.2 - 12	mg/L	D2		
Soluble Iron	ND - 3.4	mg/L	D2		
Soluble Nickel	ND - 3.3	mg/L	D2		
Specific Conductivity	285-811	umhos/cm	H		
Toluene	ND-1	µg/L	F	720	µg/L
Total Alk	22 - 230	mg/L	D2		
Total Chromium	ND - 0.04	mg/L	D2	0.1	mg/L
Total Cobalt	ND - 0.09	mg/L	D2	0.01	mg/L
Total Copper	ND - 0.13	mg/L	D2	1.3	mg/L
	ND-0.016	mg/L	F	1.3	mg/L
Total Iron	ND - 606	mg/L	D2	0.3*	mg/L
Total Lead	ND-0.22	mg/L	F	0.004	mg/L
	ND - 0.20	mg/L	D2	0.004	mg/L

TABLE A14-1. SUMMARY OF PREVIOUS DETECTIONS IN GROUNDWATER, SOIL AND SLUDGE AT THE 3M CORDOVA, ILLINOIS SITE NOT RFI-RELATED DATA

COMPOUND	CONCENTRATION RANGE	CONCENTRATION UNITS	REFERENCE	REVISED DECEMBER 1995 REGION 5 DQL/MCL	DQL/MCL UNITS
Total Nickel	ND- 0.95	mg/L	D2	0.1	mg/L
	ND-0.035	mg/L	F	0.1	mg/L
Total Organic Carbon	1.9-17.5	mg/L	H		
Total Organic Halogen	ND-1.42	mg/L	H		
Total Phosphorus	ND-4.9	mg/L	D2		
Trichloroethylene	ND-4	µg/L	F	1.6	µg/L
Xylene	ND-8.1	µg/L	I	1,400	µg/L
Zinc	ND-0.036	mg/L	F	11	mg/L
	ND - 360	mg/L	D2	11	mg/L
Soil Data					
Bray-Phosphorous	1.2-300	mg/kg	D3		
Chlorine	ND-195	mg/kg	D3		
Extractable Aluminum	26-1,600	mg/kg	D3		
Extractable Cadmium	ND-0.75	mg/kg	D3		
Extractable Chromium	ND-1.66	mg/kg	D3		
Extractable Iron	0.2-882	mg/kg	D3		
Extractable Lead	ND-6.5	mg/kg	D3		
Extractable Mercury	ND-0.3	mg/kg	D3		
Extractable Nickel	ND-46	mg/kg	D3		
Extractable Zinc	ND-17	mg/kg	D3		
ExtractableCobalt	ND-100	mg/kg	D3		
ExtractableCopper	ND-61	mg/kg	D3		
Extractable Fluoride	ND-68	mg/kg	D3		
Extractable Manganese	16-35	mg/kg	D3		
Nitrate	ND-80	mg/kg	D3		
Nitrite	ND-20.1	mg/kg	D3		
Total Cadmium	ND-0.6	mg/kg	D3	38	mg/kg
Total Chromium	7.7-66	mg/kg	D3	210	mg/kg
Total Cobalt	ND-1,600	mg/kg	D3	NA	mg/kg
Total Copper	3-33	mg/kg	D3	2,800	mg/kg
Total Flouride	68-39,800	mg/kg	D3		
Total Iron	7,000-110,000	mg/kg	D3		
Total Lead	ND-30	mg/kg	D3	400	mg/kg
Total Mercury	ND-0.27	mg/kg	D3	23	mg/kg
Total Nickel	9-390	mg/kg	D3	1,500	mg/kg
Total Phosphorous	148-674	mg/kg	D3		
Total Zinc	12-120	mg/kg	D3	23,000	mg/kg
Crop Data					
Aluminum	ND-95	mg/kgd	D4		
Antimony	ND-0.14	mg/L	D4	0.015	mg/L
	ND-0.14	mg/kgd	D4	31	mg/kg
Arsenic	ND-0.07	mg/L	D4	0.000038	mg/L
	ND-0.83	mg/kgd	D4	0.32	mg/kg
Barium	ND-5.2	mg/kgd	D4	5,300	mg/kg
Bray-Phosphorous	0.56-611.00	mg/kgd	D4		

TABLE A14-1. SUMMARY OF PREVIOUS DETECTIONS IN GROUNDWATER, SOIL AND SLUDGE AT THE 3M CORDOVA, ILLINOIS SITE NOT RFI-RELATED DATA

COMPOUND	CONCENTRATION RANGE	CONCENTRATION UNITS	REFERENCE	REVISED DECEMBER 1995 REGION 5 DQL/MCL	DQL/MCL UNITS
Cadmium	ND-12	mg/kgd	D4	38	mg/kg
	ND-0.6	mg/L	D4	0.018	mg/L
CEC(meq)	ND-42.1	mg/kgd	D4		
Chromium	ND-61	mg/L	D4	0.18	mg/L
	ND-67	mg/kgd	D4	210	mg/kg
Cobalt	ND-1,400	mg/kgd	D4	NA	mg/kg
	ND-560	mg/L	D4	NA	
Copper	ND-9.9	mg/L	D4	1.4	mg/L
	ND-60	mg/kgd	D4	2,800	mg/kg
Cyanide	ND-0.95	mg/L	D4	0.0062	mg/L
Dissolved Cadmium	ND-0.396	mg/kgd	D4		
Dissolved Chromium	ND-1.57	mg/kgd	D4		
Dissolved Cobalt	ND-100.00	mg/kgd	D4		
Dissolved Copper	ND-61.00	mg/kgd	D4		
Dissolved Iron	0.20-882.00	mg/kgd	D4		
Dissolved Lead	ND-7.62	mg/kgd	D4		
Dissolved Nickel	ND-111.00	mg/kgd	D4		
Dissolved Zinc	ND-32.20	mg/kgd	D4		
Lead	ND-6.8	mg/L	D4	0.004	mg/L
	ND-60	mg/kgd	D4	400	mg/kg
Manganese	3-10	mg/kgd	D4		
Mercury	ND-0.58	mg/kgd	D4	23	mg/kg
	ND-0.022	mg/L	D4	0.011	mg/L
Nickel	ND-220	mg/kgd	D4	1,500	mg/kg
	ND-58	mg/L	D4	0.73	mg/L
Silver	ND-0.042	mg/L	D4	0.18	mg/L
	ND-1	mg/kgd	D4	380	mg/kg
Total Phosphorous	0.1-674.0	mg/kgd	D4		
Zinc	ND-352	mg/kgd	D4	23,000	mg/kg
	0.28-71	mg/L	D4	11	mg/L
Wastewater Effluent Data					
Acetone	69 - 16,200	µg/L	E	610	µg/L
	ND - 58,000	µg/L	J	610	µg/L
Acetophenone	ND - 14	µg/L	J	3,700	µg/L
Anthracene	30	µg/L	E	1,800	µg/L
Barium	ND - 0.011	mg/L	J	2.6	mg/L
Benzidine	400	µg/L	E		
Benzene	1 - 2.6	µg/L	E	0.39	µg/L
Bis (2-Ethylhexyl) Phthalate	5 - 45	µg/L	E	4.8	µg/L
Carbazole	5 - 18	µg/L	E		
Chloroethane, Ethyl Chloride	2.1 - 7.2	µg/L	E	710	µg/L
Chloromethane	2.1 - 8	µg/L	E	2.3	µg/L
1,2-Dichlorobenzene	1 - 2	µg/L	E	370	µg/L
1,1-Dichloroethane	1.1 - 4	µg/L	E	810	µg/L
Diethyl Pthalate	8 - 27	µg/L	E	29,000	µg/L
Dimethyl Disulfide	14	µg/L	E		

TABLE A14-1. SUMMARY OF PREVIOUS DETECTIONS IN GROUNDWATER, SOIL AND SLUDGE AT THE 3M CORDOVA, ILLINOIS SITE NOT RFI-RELATED DATA

COMPOUND	CONCENTRATION RANGE	CONCENTRATION UNITS	REFERENCE	REVISED DECEMBER 1995 REGION 5 DQL/MCL	DQL/MCL UNITS
2,4-Dimethyl Phenol	8	µg/L	E	730	µg/L
1,2-Diphenylhydrazine	7 - 160	µg/L	E		
Ethanol	4,600 - 14,000	µg/L	E		
Ethyl Benzene	1 - 10	µg/L	E	1,300	µg/L
Ethyl Ether	11 - 2,900	µg/L	E		
Isophorone	42 - 91	µg/L	E	71	µg/L
Isopropanol	50 - 12,000	µg/L	E		
MEK	67 - 240	µg/L	E	1,900	µg/L
4-Methyl-2-Pentanone	390 - 1,710	µg/L	E	2,900	µg/L
Methylene Chloride	2 - 190	µg/L	E	4.3	µg/L
2-Methylphenol	6	µg/L	E	10	µg/L
	ND - 24	µg/L	J		
Naphthalene	14 - 22	µg/L	E	240	µg/L
n-Butanol	160 - 170	µg/L	E		
Nickel	ND - 0.17	mg/L	J	730	µg/L
Phenanthrene	7 - 24	µg/L	E	NA	µg/L
Tert-Butanol	170 - 16,000	µg/L	E		
Tetrahydrofuran	72 - 5,000	µg/L	E		
Toluene	1 - 12	µg/L	E	720	µg/L
Total Fluoride	ND - 47.2	mg/L	J		
Total Organic Carbon	47.1 - 75.9	mg/L	J		
Total Suspended Solids	ND - 93.0	mg/L	J		
1,1,2-Trichloroethane	6	µg/L	E	0.2	µg/L
1,3,5-Trimethylbenzene	6 - 9	µg/L	E		
1,2,4-Trimethylbenzene	1 - 8	µg/L	E		

TABLE A14-1. SUMMARY OF PREVIOUS DETECTIONS IN GROUNDWATER, SOIL AND SLUDGE AT THE 3M CORDOVA, ILLINOIS SITE NOT RFI-RELATED DATA

COMPOUND	CONCENTRATION RANGE	CONCENTRATION UNITS	REFERENCE	REVISED DECEMBER 1995 REGION 5 DQL/MCL	DQL/MCL UNITS
Xylene	4 - 63	µg/L	E	1,400	µg/L
	3.3 - 33.3	µg/L	E	1,400	µg/L
Zinc	ND - 0.026	mg/L	J	11	mg/L

NOTES:

1). Sludge sample DQL values were assumed as groundwater when units were in mg/L and soil when in mg/kg. Soil DQLs were used for all crop data and groundwater DQLs were used for wastewater data.
2). "*" = MCLs were used for compounds for which DQLs were not available.
3). ND = Not Detected above method detection limit for specific analytical event.
4). NA = Not Applicable or Not Available.
5). Values shown for Total Phenols are for the compound phenol.

REFERENCES:

D. Sludge Incorporation Permit Monitoring Data
Metals and other inorganic parameters, 1975 to present.
(D-1) sludge
(D-2) groundwater
(D-3) soil
(D-4) crop

E. Wastewater Discharge Permit Monitoring Data
Pond #3 Effluent - Priority Pollutants
March 1992 to present.

F. Special One-Time Monitoring Event
Mag sludge, aerobic digester sludge, and monitoring wells
Priority Pollutants - December 1981

G. Soils Characterization Study
January 1986

H. Equalization Basin II RCRA Interim Status Monitoring
D018 Benzene
Groundwater Statistics

I. Equalization Basin II Closure
Appendix IX parameters for groundwater and sludge
July to November 1994
Clean closure approved by USEPA, Region 5 on March 15, 1995

J. Polishing Ponds
F039 analysis of wastewater
March 2, 1993

K. Sludge Sampling Event
December 1986

P. Sludge Sampling Event
TC Analysis
February and April 1991

TABLE A14-2. SUMMARY OF PREVIOUS DETECTIONS IN GROUNDWATER, SOIL, AND SLUDGE AT THE 3M CORDOVA, ILLINOIS SITE
RFI-RELATED DATA

COMPOUND	CONCENTRATION RANGE	CONCENTRATION UNITS	REFERENCE	REVISED DECEMBER 1995 REGION 5 DQL/MCL	DQL/MCL UNITS
Groundwater Data					
Aluminum	ND - 1.4	mg/L	B		
Barium	0.036 - 0.22	mg/L	B	2.6	mg/L
Boron	ND - 0.24	mg/L	B		
Calcium	37.1 - 72.2	mg/L	B		
Cobalt	ND - 0.077	mg/L	B	NA	mg/L
Cyanide, Tot.	ND - 0.11	mg/L	B	0.0062	mg/L
Fluoride	ND - 4.3	mg/L	B	0.310*	mg/L
Iron	ND - 0.82	mg/L	B	0.30*	mg/L
Magnesium	13.4 - 25.0	mg/L	B		
Manganese	ND - 15.6	mg/L	B		
Nickel	ND - 0.13	mg/L	B	0.73	mg/L
Nitrate as N	2.40 - 52.2	mg/L	B	10*	mg/L
Potassium	ND - 41.2	mg/L	B		
Sodium	6.2 - 54.6	mg/L	B		
Strontium	0.080 - 0.35	mg/L	B		
Zinc	ND - 0.046	mg/L	B	11	mg/L
Soil Data					
Antimony	ND	mg/kg	B	31	mg/kg
Arsenic	ND - 3.6	mg/kg	B	0.32	mg/kg
Barium	24 -150	mg/kg	B	5,300	mg/kg
Beryllium	ND - 0.6	mg/kg	B	0.14	mg/kg
Cadmium	ND	mg/kg	B	38	mg/kg
Chromium (6+)	ND	mg/kg	B		mg/kg
Chromium (Tot)	7.1 - 31	mg/kg	B	0.18	mg/kg
Cobalt	ND - 7	mg/kg	B	NA	mg/kg
Copper	5.5 - 12	mg/kg	B	2,800	mg/kg
Lead	ND - 12	mg/kg	B	400	mg/kg
Nickel	10 - 20	mg/kg	B	1,500	mg/kg
Silver	ND	mg/kg	B	380	mg/kg
Strontium	11 - 32	mg/kg	B		
Thallium	ND	mg/kg	B	6.1	mg/kg
Tin	ND	mg/kg	B	46,000	mg/kg
Vanadium	11 - 69	mg/kg	B	540	mg/kg
Zinc	10 - 36	mg/kg	B	23,000	mg/kg
Sludge Data					
Acetaldehyde	ND - 0.88	mg/kg	A		
Arsenic	ND - 0.13	mg/L	C-2	0.000038	mg/L
Barium	0.33 - 0.53	mg/L	C-1	2.6	mg/L
	0.036 - 0.43	mg/L	C-2	2.6	mg/L
Benzene	ND - 0.0064	mg/L	C-2	0.00039	mg/L
	ND - 0.0063	mg/L	C-1	0.00039	mg/L
	ND - 0.010	mg/kg	A	1.4	mg/kg

TABLE A14-2. SUMMARY OF PREVIOUS DETECTIONS IN GROUNDWATER, SOIL, AND SLUDGE AT THE 3M CORDOVA, ILLINOIS SITE RFI-RELATED DATA

COMPOUND	CONCENTRATION RANGE	CONCENTRATION UNITS	REFERENCE	REVISED DECEMBER 1995 REGION 5 DQL/MCL	DQL/MCL UNITS
Bis(2-Ethyl Hexyl)Phthalate	ND - 0.50	mg/kg	A	32	mg/kg
2-Butanone	ND - 0.25	mg/L	C-1	2.5	mg/L
Carbon Disulfide	ND - 0.039	mg/kg	A	53	mg/kg
Chlorobenzene	ND - 0.012	mg/L	C-2	0.039	mg/L
Ethyl Benzene	ND - 0.006	mg/kg	A	2,900	mg/kg
Fluoranthene	ND - 0.34	mg/kg	A	2,600	mg/kg
Fluorene	ND - 1.1	mg/kg	A	300	mg/kg
Fluoride	1,200 - 5,800	mg/kg	A		
Lead	ND - 0.088	mg/L	C-2	0.004	mg/L
3/4-Methylphenol	ND - 0.021	mg/L	C-1	NA	mg/L
	ND - 0.14	mg/L	C-2	NA	mg/L
Phenanthrene	0.026 - 5.6	mg/kg	A	NA	mg/kg
Phenol	ND - 0.072	mg/kg	A	39,000	mg/kg
Pyrene	ND - 0.53	mg/kg	A	2,000	mg/kg
Tetrachloroethene	ND - 0.0071	mg/L	C-2	0.0011	mg/L
Toluene	ND - 1.0	mg/kg	A	1,900	mg/kg
Xylene	ND - 0.10	mg/kg	A	980	mg/kg

NOTES:

1) Sludge sample Data Quality Level (DQL) values were assumed as groundwater when units were in mg/L and soil when units were in mg/kg.
2) Maximum Contaminant Levels (MCLs) from the National Primary Drinking Water Regulations were used for compounds for which DQLs were not available.
3) ND = not detected above method detection limit for specific analytical event
4) * = MCLs were used for compounds for which DQLs were not available.
5) NA = Revised DQL value Not Available.

REFERENCES:

(A) May 1987 Appendix VIII sampling event
Pond #1 and #2 sludge, Mag sludge, and Aerobic Digestor sludge
Appendix VIII parameters SW-846

(B) 1989 Abbreviated RFI
Groundwater, soil, and sludge
Appendix IX parameters SW-846

(C) (Part B Permit requirement)
Sludges in all 6 surface impoundments tested for RCRA hazardous characteristics. SW-846
(C-1) November 1993
(C-2) June 1994